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1

Some Basic Concepts and Mole Concept

OVERVIEW

1. Mole concept and equivalent concept:

a. For elements:

$$1 \text{ g atom} = N \text{ atoms} = 6.023 \times 10^{23} \text{ atoms} \\ = \text{Gram atomic weight}$$

For example,

$$1 \text{ g atom of oxygen} = N_A \text{ atoms of oxygen} \\ = 6.023 \times 10^{23} \text{ atoms of oxygen} = 16 \text{ g}$$

Gram atomic weight: It is the weight of N_A atoms in grams.

$$\text{Weight of one oxygen atom} = 16 \text{ amu} \\ = 16 \times 1.66 \times 10^{-24} \text{ g}$$

$$\therefore \text{Weight of } N_A \text{ oxygen atom} = 16 \times 1.66 \times 10^{-24} \\ \times 6.023 \times 10^{23} \text{ g} \\ = 16 \text{ g}$$

where N_A is Avogadro's number.

b. For compounds:

$$1 \text{ g molecule or 1 mole} = N_A \text{ molecules} \\ = 6.023 \times 10^{23} \text{ molecules} \\ = \text{g molecular weight}$$

$$1 \text{ mol of } O_2 = N_A \text{ molecules of } O_2 \\ = 6.023 \times 10^{23} \text{ molecules of } O_2 \\ = 32 \text{ g}$$

Gram molecular weight: It is the weight of N_A molecules in grams.

$$\text{Weight of one } O_2 \text{ molecules} = 32 \text{ amu} \\ = 32 \times 1.66 \times 10^{-24} \text{ g}$$

$$\text{Therefore, Weight of } N_A \text{ molecules } O_2 \\ = 32 \times 1.66 \times 10^{-24} \times 6.023 \times 10^{23} \\ = 32 \text{ g}$$

Avogadro's hypothesis: Equal volumes of gases or vapours obeying gas laws under similar conditions of P and T contain equal number of molecules.

The statement reveals the following facts:

- One mole of gases contain N_A molecules.
- The volume of 1 mol gas at NTP or STP has 22.4 L.
- Gram molecular weight for a gas is the weight of its 22.4 L at NTP.
- NTP refers $P = 1 \text{ atm}$ and $T = 0^\circ\text{C}$ or 273 K .

$$e. \text{ Molecular weight of a gas} = 2 \times \text{Vapour density of gas}$$

$$f. \text{ Avogadro's number} = 6.023 \times 10^{23}$$

– Number of atoms in 1 g atom of an element

– Number of molecules in 1 mole of compound

3. Dulong and Petit's law:

$$\text{Atomic weight} \times \text{Specific heat} \approx 6.4 \text{ (for metals only)}$$

Specific heat in cal g^{-1} .

4. Equivalent weight: Equivalent weight of a substance depends upon the nature of chemical reactions in which the substance takes part. The evaluation of equivalent weight of a substance may therefore be cautiously made.

a. Equivalent weight of an element in a redox change

If the substance takes part in a redox change, its equivalent weight should be reported only by

Equivalent weight of a compound

$$= \frac{\text{Molecular weight}}{\text{Number of electrons lost or gained during redox change by one molecule of that compound}}$$

Equivalent weight of an element

$$= \frac{\text{Atomic weight}}{\text{Number of electrons lost or gained during redox change by one atom of that compound}}$$

b. Equivalent weight of an element or compound in a non-redox change

i. Equivalent weight of an element

$$= \frac{\text{Atomic weight of element}}{\text{Valency of element}}$$

ii. Equivalent weight of a compound

$$= \text{Ew of I part} + \text{Ew of II part}$$

The above two equations are not valid for hydrated compounds. Also, equivalent weight of a compound

$$= \frac{\text{Atomic weight of compound}}{\text{Total charge on cationic or its ionic part}}$$

For example,

1. NaCl

$$Ew_{NaCl} = 23 + 35.5 = 58.5$$

$$Ew_{NaCl} = \frac{Mw \text{ of NaCl}}{1} = \frac{58.5}{1} = 58.5$$

2. AlCl₃

$$Ew_{AlCl_3} = Ew_{Al^{3+}} + Ew_{Cl^-}$$

$$= \frac{27}{3} + 35.5 = 44.5$$

$$Ew_{AlCl_3} = \frac{Mw \text{ of AlCl}_3}{3} = \frac{133.5}{3} = 44.5$$

3. K₂SO₄·Al₂(SO₄)₃·24H₂O: (Total charge = +8 or -8)

$$Ew_{Alum} = \frac{M}{8}$$

c. Equivalent weight of an acid or base.

$$Ew_{Acid} = \frac{Mw_{acid}}{\text{Basicity}} \quad (\text{Basicity is number of H atoms replaced from one molecule of acid})$$

$$Ew_{Base} = \frac{Mw_{base}}{\text{Acidity}} \quad (\text{Acidity is the number of H atoms replaced from acid by one molecule of base})$$

For example,



$$\text{Basicity} = 2 \quad \text{Acidity} = 1$$

$$\therefore E_{H_3PO_3} = \frac{M}{2} \quad E_{NaOH} = \frac{M}{1}$$

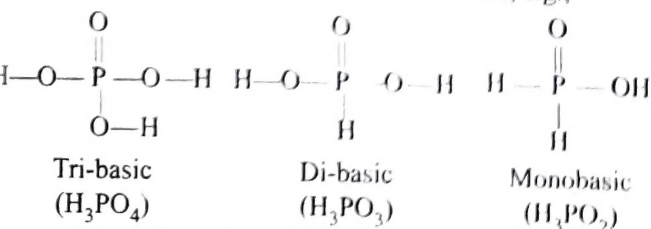
d. Equivalent weight of an ion:

$$\text{Equivalent weight of ion} = \frac{\text{Formula weight of ion}}{\text{Charge on ion}}$$

e. Equivalent weight of acid salt:

$$\text{Equivalent weight of ion} = \frac{\text{Formula weight of ion}}{\text{Replaceable H atoms in it}}$$

An acid salt is one which has replaceable H atoms, e.g., NaHCO₃, NaHSO₄, Na₂HPO₄. However, Na₂HPO₃ is not an acid salt since it does not have replaceable H atom because H₃PO₃ is dibasic acid. In oxy acids, only those H atoms are replaceable which are attached on O atom, e.g.,



Normality: It is defined as number of equivalents of a solute present in one litre of solution.

$$N = \frac{\text{Equivalent of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Weight of solute}}{\text{Equivalent weight of solute} \times V_{\text{sol}} \text{ (in L)}}$$

$$N = \frac{W}{E \times V_{\text{sol}} \text{ (in L)}} = \frac{W \times 1000}{E \times V_{\text{sol}} \text{ (in mL)}}$$

$$\text{Also, equivalent} = N \times V_{\text{sol}} \text{ (in L)}$$

$$= \frac{\text{Weight of solute}}{\text{Equivalent weight of solute}}$$

$$\text{and milli equivalent} = N \times V_{\text{sol}} \text{ (in mL)}$$

$$= \frac{\text{Weight of solute}}{\text{Equivalent weight of solute}} \times 1000$$

6. **Molarity:** It is defined as the moles of solute present in one litre of solution.

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Weight of solute}}{\text{Molecular weight of solute} \times V_{\text{sol}} \text{ (in L)}}$$

$$= \frac{\text{Weight of solute} \times 1000}{\text{Molecular weight of solute} \times V_{\text{sol}} \text{ (in mL)}}$$

$$M = \frac{W \times 1000}{Mw \times V \text{ (mL)}}$$

$$\text{Also, mole of solute} = M \times V_{\text{sol}} \text{ (in L)}$$

$$= \frac{\text{Weight of solute}}{\text{Molecular weight of solute}}$$

$$= M \times V \text{ (in mL)} = \frac{W}{Mw} \times 1000$$

Note: a. Moles and milli moles react according to equation.

$$\text{b. } \therefore \text{Molarity} = \frac{\text{Moles}}{V \text{ (in L)}}$$

$$\text{Normality} = \frac{\text{Equivalent}}{V \text{ (in L)}}$$

$$\therefore \frac{M}{N} = \frac{\text{Moles}}{\text{Equivalent}} = \frac{W \times Ew}{Mw \times W} = \frac{Ew}{Mw}$$

$$= \frac{1}{\text{Valency factor}}$$

$$\therefore \text{Normality} = \text{Molarity} \times \text{Valency factor}$$

c. It is better to solve a numerical by equivalent or mEq rather than using moles and milli moles. For this purpose, molarity should be changed into normality according to the above equation.

7. **Molality:** Moles of solute present in 1 kg of solvent.

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Weight of solvent in kg}}$$

$$= \frac{\text{Weight of solute}}{M_w \text{ of solute} \times \text{Weight of solvent in kg}}$$

$$= \frac{\text{Weight of solute} \times 1000}{M_w \text{ of solute} \times \text{Weight of solvent in g}}$$

Weight of solvent = Weight of solution – Weight of solute

8. **Strength of solution:** Amount of solute present in one litre solution.

$$S = \frac{\text{Weight of solute}}{\text{Volume of solution in litre}} = \frac{W}{V_{\text{sol}} \text{ (in L)}}$$

$$N = \frac{W}{E_w} \times \frac{1}{V_{\text{sol}} \text{ (in L)}}$$

$$\therefore S = N \times E_w$$

9. **In terms of percentage:**

$$\% \text{ by weight} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

$$\% \text{ by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

$$\% \text{ by (W/V)} = \frac{\text{Weight of solute}}{\text{Volume of solution}} \times 100$$

For example, a solution is 35% by weight.

W_2/W_s means: 100 g solution contains 35 g solute

35% by volume: 100 mL solution contains 35 mL solute

35% by strength (W/V): 100 mL solution contain 35 g solute

10. **Mole fraction:** Mole fraction of solvent (χ_A)

$$= \frac{\text{Moles of solvent}}{\text{Moles of solute} + \text{moles of solvent}} = \frac{n_A}{n_A + n_B}$$

Mole fraction of solvent (χ_B)

$$= \frac{\text{Moles of solvent}}{\text{Moles of solute} + \text{Moles of solvent}} = \frac{n_B}{n_A + n_B}$$

By the two equations above,

$$\therefore \chi_A + \chi_B = 1$$

$$\therefore \frac{\chi_A}{\chi_B} = \frac{n_A}{n_B}$$

12. Action of heat of some important compounds:

	Alkali metals	Alkaline earth metals
Sulphates	Stable $\text{Na}_2\text{SO}_4 \xrightarrow{\Delta} \text{No reaction}$	Stable $\text{CaSO}_4 \xrightarrow{\Delta} \text{No reaction}$
Carbonates	Stable $\text{K}_2\text{CO}_3 \xrightarrow{\Delta} \text{No reaction}$ But Li_2CO_3 is unstable. $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2$	Unstable $\text{MgCO}_3 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2$
Bicarbonates	Unstable $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	Unstable $\text{Ca}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{CaO} + \text{H}_2\text{O} + 2\text{CO}_2$

11. Some important formulae:

a. Molarity (M) = $\frac{W_2 \times 1000}{M_{w_2} \times V \text{ of solution in mL}}$

b. Molality (m) = $\frac{W_2 \times 1000}{M_{w_2} \times W_1 \text{ (Weight of solvent in g)}}$

c. Normality (N) = $\frac{W_2 \times 1000}{E_{w_2} \times V \text{ of solution in mL}}$

d. Normality = 'n' factor \times M

n implies:

i. Basicity of an acid (i.e., replaceable H^+ ions)

ii. Acidity of base (i.e., replaceable OH^- ions)

iii. Total +ve or -ve charge in case of salt

iv. Number of electrons involved in redox reactions

e. $M = \frac{\% \text{ by weight} \times 10 \times \text{Density of solution}}{M_{w_2}}$

f. $m = \frac{n_2 \times 1000}{n_1 \times M_{w_1}} = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}}$

g. $d = M \left(\frac{M_{w_2}}{1000} + \frac{1}{m} \right)$

h. $\chi_1 = \frac{n_1}{n_1 + n_2} = \frac{\frac{W_1}{M_{w_1}}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}}}$

$$\chi_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{W_2}{M_{w_2}}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}}}$$

or ($\chi_2 = 1 - \chi_1$)

i. $X_1 = \frac{W_1}{W_1 + W_2}$ $X_2 = \frac{W_2}{W_1 + W_2}$

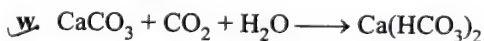
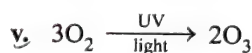
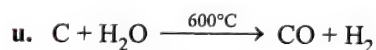
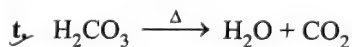
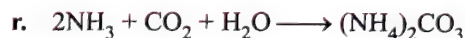
or ($X_2 = 1 - X_1$)

j. $\text{ppm} = \frac{W_2}{W_{\text{sol}}} \times 10^6$

Nitrates	Unstable $2\text{KNO}_3 \xrightarrow{\Delta} 2\text{KNO}_2 + \text{O}_2$ But LiNO_3 decomposes differently, like alkaline earth metal nitrates $2\text{LiNO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + 2\text{NO}_2 + \text{O}_2$	Unstable $2\text{CaNO}_3 \xrightarrow{\Delta} 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$
Hydroxides	Stable $\text{NaOH} \xrightarrow{\Delta} \text{No reaction}$ But hydroxides of Li decomposes, such as alkaline earth metal hydroxides $2\text{LiOH} \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{H}_2\text{O}$	Unstable $\text{Mg(OH)}_2 \xrightarrow{\Delta} \text{MgO} + \text{H}_2\text{O}$
Formation of Nitrides	Alkali metals except Li do not react with N_2 $\text{Na} + \text{N}_2 \xrightarrow{\Delta} \text{No reaction}$ Li forms nitrides with N_2 $6\text{Li} + \text{N}_2 \xrightarrow{\Delta} 2\text{Li}_3\text{N}$	The alkaline earth elements burn in N_2 to form ionic nitrides with formula M_3N_2 $3\text{Ca} + \text{N}_2 \longrightarrow \text{Ca}_3\text{N}_2$

13. Some basic chemical reactions:

- a. $2\text{KClO}_3 \xrightarrow{\Delta} 2\text{KCl} + 3\text{O}_2$
- b. $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
- c. $\text{NaNO}_3 \xrightarrow{\Delta} \text{NaNO}_2 + \frac{1}{2}\text{O}_2$
- d. $2\text{Pb(NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$
- e. $\text{Na}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}$
- f. $2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$
- g. $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
- h. $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
- i. $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$
- j. $2\text{AgNO}_3 \xrightarrow{\Delta} 2\text{Ag} + \text{NO}_2 + \text{O}_2$
- k. $2\text{Mg} + \text{O}_2 \longrightarrow 2\text{MgO}$
- l. $3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
- m. $4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$
- n. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
- o. $2\text{H}_2\text{O}_2 \xrightarrow{\Delta} 2\text{H}_2\text{O} + \text{O}_2$
- p. $2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + \text{O}_2$
- q. $\text{K}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{KCl} + \text{CO}_2 + \text{H}_2\text{O}$



14. Some general points:

- a. Molality, % by weight, mole fraction are independent of temperature since they involve weights.
- b. Normality, molarity, percent by volume; percent by strength, and strength are temperature dependent and normally decrease with increase in temperature since the volume of solution increases with T .
- c. Sometimes, the term formality is used in place of molarity.
- d. Normal, molar solution means solutions having normality 1 N and molarity 1 M, respectively.
- e. Standard solution is one whose N or M is known.
- f. During the dilution of a solution, equivalent, molar equivalent, mole, or millimoles of a solute do not change; however, N and M change.

1.1 INTRODUCTION

Chemistry is the science of atoms and molecules and their transformations. It is the science of the infinite number of molecules that are built from these atoms.

Chemistry plays an important role in daily life. Chemical principles are important in a plethora of areas such as weather patterns, functioning of brain, and operation of a computer. Chemicals are used in manufacturing acids, alkalis, salts, dyes, drugs, polymers, soaps, detergents, metals, alloys, fertilizers, insecticides, pesticides, and other inorganic and organic chemicals. Chemicals also constitute food, health care products, and other materials which improve the quality of life. Some life-saving drugs, such as *cisplatin* and *taxol* are effective in cancer therapy and AZT (azidothymidine) is used for helping AIDS victims, have been isolated from plants and animal sources or prepared by synthetic methods.

Chemical principles help in designing and synthesising new materials having specific magnetic, electrical, and optical properties, which further help in manufacturing optical fibres, super-conducting ceramics, conducting polymers, and solid state devices. These principles also help in synthesising safer alternatives to environmentally hazardous refrigerants such as CFCs (chloro fluoro carbons) responsible for ozone depletion in the stratosphere. Moreover, some of the intellectual challenges for the future chemists are yet to be solved such as management of green house gases such as methane, carbon dioxide, etc., understanding bio-chemical processes, use of enzymes for large-scale production of chemicals, and synthesis of new toxic materials.

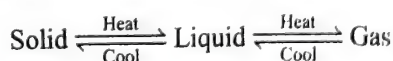
1.2 MATTER

Matter is anything that occupies mass and space. It exists in three physical states, e.g., *solid*, *liquid*, and *gas*. In solids, the constituent particles are held very close to each other in an orderly manner with not much freedom of movement. In liquids, the constituent particles are close to each other but they can move around. However, in gases, the constituent particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast.

Characteristics:

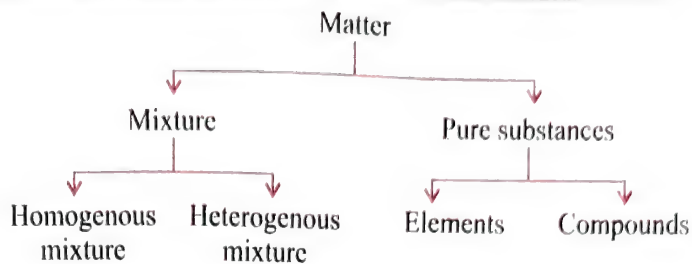
- Solids have definite volume and definite shape.
- Liquids have definite volume but not definite shape. They take the shape of the container in which they are kept.
- Gases have neither definite volume nor definite shape. They occupy completely the container in which they are kept.

These three states are interconvertible on changing the conditions of temperature and pressure.



1.2.1 CLASSIFICATION OF MATTER

Matter can be classified broadly as mixture or pure substances, which can be further subdivided as shown below.



- Mixture:** A mixture contains two or more substances present in it in any ratio which are called its components. For example, sugar solution in water, air, tea, etc.
- Homogenous mixture:** A mixture in which the components completely mix with each other and its composition is uniform throughout. For example, salt solution, sugar solution, air, etc.
- Heterogenous mixture:** A mixture in which the composition is not uniform throughout, and different components sometimes can be observed. For example, mixture of salt and sugar, grains and pulses alongwith some dirt (often stone) pieces, etc. Components of a mixture can be separated by physical methods such as mechanical separation, hand picking, filtration, crystallisation, distillation, fractional distillation, steam distillation, etc.
- Pure substances:** They have fixed composition, whereas mixture may contain the components in any ratio and its composition is variable. For example, gold, silver, copper, water, glucose, etc. Water contains hydrogen and oxygen in a fixed ratio and has fixed constituents. The constituents of pure substances cannot be separated by physical methods. Pure substance can be classified further into elements and compounds.
- Element:** It consists of only one type of particles, atoms or molecules. For example, silver, copper, sodium, hydrogen, oxygen, etc. They all contain atoms of one type. However, the atoms of different elements are different in nature.
- Molecule:** Two or more atoms combine to give molecules of the element. Hydrogen, oxygen, and nitrogen gases consists of molecules in which atoms of same elements combine to give their respective molecules.
- Compound:** When two or more atoms of different elements combine, the molecule of a compound is formed. For example, water ammonia, carbon monoxide, sodium chloride, etc.

The atoms of different elements are present in a compound in a fixed and definite ratio, and this ratio is a characteristic of a particular compound. The properties of a compound are different from those of its constituent elements. For example, hydrogen and oxygen are gases whereas the compound formed by their combination, i.e., water, is a liquid. Hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher.

The constituents of a compound cannot be separated into simpler substances by physical methods, but they can be separated by chemical methods.

1.2.2 PROPERTIES OF MATTER AND THEIR MEASUREMENTS

The properties of a substance have unique characteristics and are classified into physical and chemical properties.

- a. Physical properties:** Those properties which can be measured or observed without changing the identity or composition of the substance are known as physical properties, e.g., colour, melting point, boiling point, odour, etc.
- b. Chemical properties:** Those properties which describe a matter's 'potential' to undergo some chemical changes are known as chemical properties, e.g., characteristics reactions of different substances which include acidity or basicity, combustibility, etc.
- c. Measurement:** Any quantitative observation represented by a number followed by a unit in which it is measured is called measurement, such as length, area, volume, etc.

For example, length of a room is 10 m; here 10 is the number and m denotes metre—the unit in which the length is measured.

Two different systems of measurement, i.e., the *English system* and the *metric system* are used. The metric system, originated in France in late 18th century, is more convenient and widely used. This system is based on the decimal system.

1.3 THE INTERNATIONAL SYSTEM OF UNITS (SI)

The international system of units (in French, Le System International d'unités—abbreviated as SI) was established at the 11th General Conference of Weights and Measures (CGPM—Conference Generale des Poids et Mesures). The CGPM is an inter governmental treaty organisation created by a diplomatic treaty known as Metre convention which was signed in Paris in 1875.

The SI system has seven base units and is shown in Table 1.1. The definitions of the SI base units are given in Table 1.4.

These base units pertain to seven fundamental scientific quantities. The other physical quantities such as volume, density, velocity, etc., can be derived from these seven fundamental quantities (Table 1.3). The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit (Tables 1.1–1.4).

Table 1.1 SI base units

Base physical quantity and symbol for quantity	Name of the Unit	Symbol
Mass (<i>m</i>)	kilogram	kg
Length (<i>l</i>)	metre	m
Time (<i>t</i>)	second	s
Temperature (<i>T</i>)	kelvin	K
Electric current (<i>I</i>)	ampere	A
Luminous intensity (<i>I_v</i>)	candela	cd
Amount of substance (<i>n</i>)	mole	mol

Table 1.2 SI prefixes

Multiple	Prefix	Symbol
10^{24}	yotta	Y
10^{21}	zetta	Z
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^2	hecto	h
10	deca	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y

Table 1.3 Derived units

Quantity	Definition of quantity	Expression in terms of SI base units
Area	Length squared	m^2
Volume	Length cubed	m^3
Density	Mass per unit volume	kg/m^3 or $kg\ m^{-3}$
Velocity	Distance travelled per unit time	m/s or $m\ s^{-1}$
Acceleration	Velocity changed per unit time	m/s^2 or $m\ s^{-2}$
Force	Mass times acceleration of object	$kg\ m/s^2$ or $kg\ m\ s^{-2}$ (newton, N)
Pressure	Force per unit area	$kg/(m\ s^2)$ or $kg\ m^{-1}\ s^{-2}$ (pascal, Pa)
Energy (work, heat)	Force times distance travelled	kg^2/s^2 or $kg\ m^2\ s^{-2}$ (joule, J)
Electric charge	Ampere times second (As)	(Coulomb, C)
Electric potential	Energy per unit charge	$J\ A^{-1}\ s^{-1}$ potential difference (volt, V)

Table 1.4 Definition of SI base units

Unit	Symbol	Definition
Mass	Kilogram (kg)	It is equal to the mass of Pt-Ir cylinder that is stored in an airtight jar at the International Bureau of Weights and Measures in Sèvres, France. or It is equal to the mass of the international prototype of the kilogram.
Length	Metre (m)	It is the length of the path travelled by light in vacuum during a time interval of $1/299,792,458$ of a second.
Time	Second (s)	It is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between two hyper fine levels of the ground state of the Caesium-133 atom.
Amount of the substance	Mole (n)	It is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kg of C-12. The elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified group of such particles.
Thermodynamic temperature	Kelvin (K)	It is the fraction of $1/273.16$ of the thermodynamic temperature of the triple point of water.
Electric current	Ampere (A)	It is the current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross section and placed 1 metre apart in vacuum, would produce a force equal to 2×10^{-7} newton per metre of length.
Luminous intensity	Candela (cd)	It is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of $1/683$ watt per steradian.

1.3.1 DERIVED UNITS

The units of all other physical quantities are derived out of those of the basic physical quantities the units thus obtained are called derived units. Some physical quantities and their derived units are given in Table 1.3.

1.3.2 SUBSIDIARY UNITS

Sometimes we require units that may be multiples or fractions of the base units. The SI system recommends multiples such as 10^3 , 10^6 , 10^9 etc. and fractions such as 10^{-3} , 10^{-6} , 10^{-9} etc., i.e., the powers are the multiples of 3. These are indicated by special prefixes and are given in Table 1.2.

1.3.3 MASS AND WEIGHT

Mass of a substance is the amount of matter contained in it whereas weight is the force exerted by gravity on a substance. The mass of a substance is constant while its weight changes from one place to another due to variation in gravity.

The mass of a substance is measured by using an analytical balance. The SI unit of mass is kilogram. Due to smaller amount of substance used in chemical reaction, fraction of kilogram, i.e., gram, is used ($1 \text{ kg} = 1000 \text{ g}$).

a. Volume: Unit of volume is $(\text{length})^3$. SI unit of volume is m^3 , for smaller volumes, cm^3 or dm^3 units are used.

Another unit, litre (L), which is not an SI unit, is used for measurement of volume of liquids.

$$1 \text{ L} = 1000 \text{ mL}$$

$$1000 \text{ cm}^3 = 1 \text{ dm}^3 = 1 \text{ L}$$

Volume of liquids or solutions is measured by using burette, pipette, graduated cylinder, or volumetric flask.

b. Density: Density of a substance is mass per unit volume.

$$\begin{aligned} \text{SI unit of density} &= \frac{\text{SI unit of mass}}{\text{SI unit of volume}} \\ &= \frac{\text{kg}}{\text{m}^3} \text{ or } \text{kg m}^{-3} \end{aligned}$$

For smaller units of density, g cm^{-3} is used, where mass is expressed in g and volume is expressed in cm^3 .

c. Temperature: Temperature of a substance is measured in three common scales, i.e., $^{\circ}\text{C}$ (degree Celsius), $^{\circ}\text{F}$ (degree Fahrenheit) and K (Kelvin). K is the SI unit. The temperatures $^{\circ}\text{F}$ and $^{\circ}\text{C}$ are related to each other by the following relationship:

$$^{\circ}\text{F} = \frac{9}{5}(^{\circ}\text{C}) + 32$$

The Kelvin scale is related to Celsius scale as follows

$$K = ^\circ C + 273.15$$

Temperature below 0°C (i.e., negative values) is possible in Celsius scale, but in Kelvin scale, negative temperature is not possible.

- d. **Reference standard:** The mass standard is kilogram (kg) since 1889. It is defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at the International Bureau of Weights and Measures in Sèvres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attacks and its mass does not change for long time.

A new standard of mass focuses to measure accurately the number of atoms in a well-defined mass of sample. In this method, X-rays were used to determine the atomic density of an ultrapure silicon crystal, which has an accuracy of about 1 part in 10^6 but has not been adopted as a standard yet.

The metre standard is defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0°C (273.15 K) in the International Bureau of Weights and Measures, Sèvres, France.

In 1960, the length of metre was defined as 1.65076373×10^6 times the wavelength of light emitted by a krypton laser.

The metre standard was defined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of $1/299\,792\,458$ of a second.

Similar to length and mass, there are reference standards for other physical quantities also.

1.4 UNCERTAINTY IN MEASUREMENT

In the study of chemistry, the theoretical as well as experimental data has to be presented with certainty. Thus, there are meaningful ways to handle the numbers conveniently and present the data realistically with certainty to the extent possible.

1.4.1 SCIENTIFIC NOTATION

[illegible]

For such numbers, scientific notation is used, i.e., exponential notation in which any number can be represented in the form of $N \times 10^n$, where n is an exponent having positive or negative values and N can vary between 1 and 10.

Thus, 543.609 can be written in scientific notation as 5.43609×10^2 . In this operation decimal had to be moved to the left by two places and same is the exponent (2) of 10 in the scientific notation.

Similarly, 0.00027 can be written as 2.7×10^{-4} . Here, the decimal had to be moved four places to the right and same is the exponent (-4) of 10 in the scientific notation.

1.4.2 MULTIPLICATION AND DIVISION

The above two operations follow the same rules, i.e.,

$$(4.6 \times 10^6)(3.9 \times 10^9) = (4.6 \times 3.9)(10^{6+9}) = 17.94 \times 10^{15}$$

$$\begin{aligned}(5.6 \times 10^{-3})(4.7 \times 10^{-5}) &= (5.6 \times 4.7)(10^{-3+(-5)}) \\ &= 26.32 \times 10^{-8}\end{aligned}$$

$$\frac{3.8 \times 10^{-4}}{5.9 \times 10^5} = (3.8 \div 5.9) (10^{-4-5}) = 0.64406 \times 10^{-9}$$

1.4.3 ADDITION AND SUBTRACTION

For such operations, first write the numbers in such a way that they have same exponent. After that, the coefficients are added or subtracted as the case may be, for example, for addition:

$$7.65 \times 10^3 + 8.69 \times 10^4$$

$$= 0.765 \times 10^4 + 8.69 \times 10^4 \text{ (exponent is made same for both the numbers.)}$$

$$= (0.765 + 8.69) \times 10^4 = 9.455 \times 10^4$$

Similarly, subtraction of two numbers can be done as follows:

$$\begin{aligned} 5.6 \times 10^{-3} - 6.2 \times 10^{-4} &= (5.6 \times 10^{-3}) - (0.62 \times 10^{-4} \times 10^1) \\ &= (5.6 \times 10^{-3}) - (0.62 \times 10^{-3}) \\ &= (5.6 - 0.62) \times 10^{-3} = 4.98 \times 10^{-3} \end{aligned}$$

1.4.4 ACCURACY AND PRECISION

The measurement involving counting of whole numbers of identifiable objects, e.g., apples, oranges, chairs, etc., can be known accurately, i.e., they are of exact numbers. Likewise, defined quantities are also exact, e.g., there are exactly 60 min in 1 h. But many scientific experimental measurements have some amount of uncertainty associated with it. The accuracy of any such measurement depends upon.

- a. The accuracy of the instrument, i.e., measuring device.
- b. The skill of the operator.

Precision: It refers to the closeness of various measurements for the same quantity. If the values of different measurements are close to each other and hence close to their average value, the measurement is said to be precise. The average value of different measurements may not be close to the correct value. The precision depends upon the measuring device as well as the skill of the operator.

Accuracy: It is the agreement of a particular value to the true value of the result. If the average value of different measurements is close to the true value, the measurement is said to be accurate. The individual measurements may not be close to each other.

For example, if the true value for a result is 4.00 g and the observations made by four students are shown as below:

Table 1.5 Data to understand accuracy and precision

Student	Measurements (g)				
	1	2	3	4	Average
A	4.00	4.01	4.02	3.99	4.005
B	3.5	3.6	3.7	3.8	3.65
C	3.7	3.9	4.1	4.3	4.00
D	3.6	4.2	4.4	4.8	4.25

Measurement by student A is both accurate and precise.

Measurement by student B has poor accuracy but good precision.

Measurement by student C has good accuracy but poor precision.

Measurement by student D has poor accuracy and poor precision.

The results are explained diagrammatically as shown in Fig. 1.1.

A measurement having a good accuracy but poor precision of different measurements may give a correct average (though generally poor precision corresponds to poor accuracy). The reverse is not true. Good precision does not necessarily mean good accuracy. For example, length of a room of 10 m may be mistakenly taken as 20 m. Various measurements taken may have good precision, but the accuracy will be very poor. Such errors in measurement when the same mistake is made repeatedly are called *systematic errors*. They effect the accuracy of the measurement but do not affect the precision.

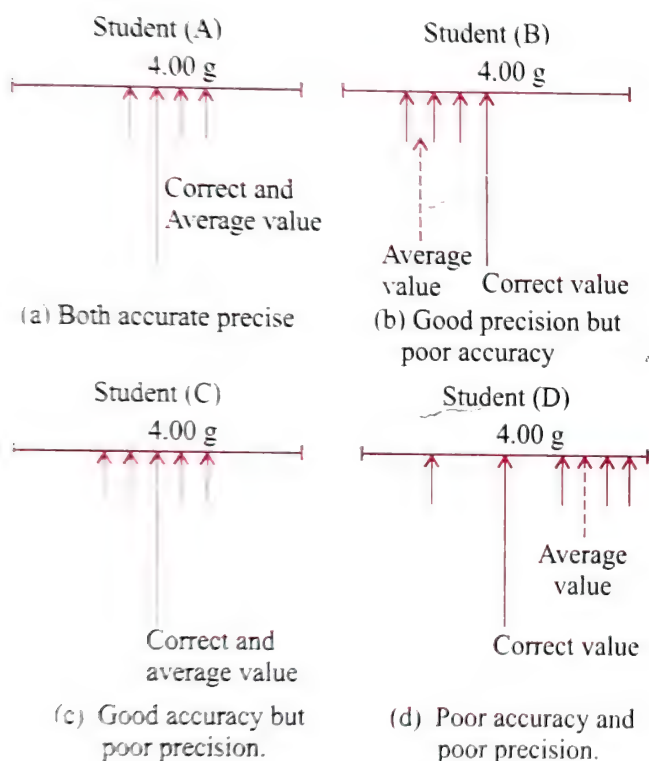


Fig. 1.1 Explanation of precision and accuracy

1.4.5 SIGNIFICANT FIGURES

The uncertainty in the experimental or the calculated value is indicated by mentioning the number of significant figures.

Significant figures are the total number of digits in a number including the last digit whose value is uncertain.

The uncertainty is indicated by writing the certain digit and the last uncertain digit. Suppose the volume of a solution is 20.5 mL, 20 is certain and 5 is uncertain and the uncertainty is ± 1 in the last digit. All measured quantities are reported in such a way that only the last digit is uncertain usually by ± 1 .

Rules for Determining the Number of Significant Figures

- All non-zero digits and zeros between non-zero digits are significant. For example,
 - 876 m has three significant figures.
 - 0.56 g has two significant figures.
 - 4006 g has four significant figures.
 - 4.06 cm has three significant figures.
- Zeros to the left of the first non-zero digit in a number are not significant. Such zeros indicate the position of decimal. For example,
 - 0.04 m has one significant figure.
 - 0.0063 kg has two significant figures.
- If a number ends in zeros but these zeros are to the right of decimal point, then these zeros are significant. For example,
 - 6.0 m has two significant figures.
 - 6.40 m has three significant figures.
 - 5.400 g has four significant figures.
 - 0.0500 kg has three significant figures.
- Zeros at the end or right of a number are significant provided they are on the right side of decimal point, otherwise the zeros are not significant. For example,
 - 0.400 g has three significant figures.
 - 200 g has only one significant figure.
- Exact numbers have an infinite number of significant figures. For example, in 4 chairs or 40 apples, there are infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing the decimal, i.e., $4 = 4.000000$ or $40 = 40.000000$.
- If a number ends in zero but these zeros are not to the right of a decimal point, then these zeros may or may not be significant, e.g., 20600 g may have three, four, or five significant figures. This ambiguity is removed by expressing the value in an exponential form. The above mass can be written in three different exponential forms known as scientific notation as follows:
 - 2.06×10^4 g has three significant figures.

or

- 2.060×10^4 g has four significant figures.

or

- 2.0600×10^4 g has five significant figures.

When numbers are written in scientific notation, the number of digits between 1 and 10 gives the number of significant figures. Thus, in such cases, the significant figures of only the first factor are counted. Note that all zeros to the right of a decimal point are significant. Thus, the general notation is $N \times 10^n$, where N a number with a single non-zero digit to the left of the decimal point and n = an integer.

The above method of expressing a number is called *exponential or scientific notation*.

Addition and Subtraction of Significant Figures

The result should not have more digits to the right of the decimal point than either of the original numbers. For example,

$$22.22$$

$$15.0$$

$$2.024$$

$$39.244$$

In the above case, 15.0 has only one digit after the decimal point. So, the result should be reported only upto one digit after decimal point and therefore the result is 39.2.

Multiplication and Division of Significant Figures

For these two operations, the result should be reported with no more significant figures as are there in the measurement with the few significant figures, e.g.,

$$4.5 \times 2.15 = 9.675$$

Since 4.5 has two significant figures, the result should not have more than two significant figures. Thus, the result is 9.6.

Similarly, for,

$$69.7 \div 4.576 = 15.2316$$

The result is 15.2.

1.4.6 ROUNDING OFF THE NUMBERS

- If the rightmost digit to be removed is more than 5, the preceding number is increased by 1, e.g., in 2.376, if 6 has to be removed, then the preceding number 7 has to be round off to 8. So, the result should be 2.38.
- If the rightmost digit to be removed is less than 5, the preceding number is not changed, e.g., in 5.464, if 4 is to be removed then the result is 5.46.
- If the rightmost digit to be removed is 5, the preceding number will not be changed if it is an even number, but it will increase by 1 if it is an odd number. For example, 7.75 is to be rounded by removing 5, increase 7 to 8 giving the result as 7.8. But if 7.85 is to be rounded off its result will be 7.8.

ILLUSTRATION 1.1

Calculate the following:

- $(6.7 \times 10^5) \times (4.6 \times 10^4)$
- $(7.6 \times 10^7) \times (3.8 \times 10^{-4})$
- $(6.8 \times 10^{-3}) \times (5.2 \times 10^{-4})$
- $(6.7 \times 10^5) \div (4.6 \times 10^4)$
- $(7.6 \times 10^7) \div (3.8 \times 10^{-4})$
- $(6.8 \times 10^{-3}) \div (5.2 \times 10^{-4})$
- $7.65 \times 10^2 + 2.72 \times 10^3$
- $7.87 \times 10^{-4} - 2.61 \times 10^{-5}$

Sol.

- $(6.7 \times 4.6) (10^{5+4}) = 30.82 \times 10^9$
- $(7.6 \times 3.8) (10^{7-4}) = 28.88 \times 10^3$
- $(6.8 \times 5.2) (10^{-3-4}) = 35.36 \times 10^{-7}$
- $\frac{6.7 \times 10^5}{4.6 \times 10^4} = \frac{6.7}{4.6} \times (10^{5-4}) = 1.456 \times 10^1 = 14.56$

$$e. \frac{7.6 \times 10^7}{3.8 \times 10^{-4}} = \frac{7.6}{3.8} \times (10^{7-(-4)}) = 2.0 \times 10^{11}$$

$$f. \frac{6.8 \times 10^{-3}}{5.2 \times 10^{-4}} = \frac{6.8}{5.2} \times (10^{-3-(-4)}) = 1.3 \times 10^1 = 13.0$$

$$g. \begin{aligned} 7.65 \times 10^2 + 2.72 \times 10^3 &= (7.65 + 2.72 \times 10^1) \times 10^2 \\ &= (7.65 + 27.2) \times 10^2 \\ &= 34.85 \times 10^2 \end{aligned}$$

$$h. \begin{aligned} (7.87 \times 10^{-4} - 2.61 \times 10^{-5}) \\ &= (7.87 \times 10^{-4} - 2.61 \times 10^{-4} \times 10^{-1}) \\ &= (7.87 \times 10^{-4} - 0.261 \times 10^{-4}) \\ &= (7.87 - 0.261) \times 10^{-4} = 7.609 \times 10^{-4} \end{aligned}$$

ILLUSTRATION 1.2

How many significant figures are there in each of the following numbers?

- π
- The sum of 16.4 + 0.3254
- The product of 12×7.435
- 0.0075
- 5.033×10^{22}
- 7.007
- 6000
- The subtraction of $19.3 - 0.4567$

Sol.

- As $\pi = \frac{22}{7} = 3.1428571\dots$, hence it has infinite number of significant figures.
- The result should have upto one decimal point as in 16.4. The sum is 16.7254. So, the result is 16.7. So, it has three significant figures.
- Two significant figures. The product is 89.22. The result is reported with least number of significant figures involved in the calculation (i.e., 12).
- Two significant figures because the zeros on the left of the first non-zero number are not significant.
- Four significant figures because the first term gives the significant figures and the exponential term is not considered.
- Four significant figures because the zeros between the non-zero digits are significant figures.
- Four significant figures. But in scientific or exponential notation significant figures vary, e.g., 6.0×10^3 has two significant figures, 6.00×10^3 or 6.000×10^3 has three or four significant numbers, respectively.
- Three significant figures because the number with least significant figures involved in the calculation (i.e., 19.3) has three significant figures.

ILLUSTRATION 1.3

What is the difference between 2.0 m and 2.00 m.

Sol. They are scientifically different although they seem to be same. 2.0 m has two significant figures and hence its precision is 0.1 part in 2, i.e., 50 ppt (parts per thousand). 2.00 m has three significant figures and its precision is 0.01 parts in 2, i.e., 5 ppt. Hence, 2.00 m is more precise measurement than 2.0 m.

ILLUSTRATION 1.4

Express the result of the following data to the appropriate number of significant figures.

$$\frac{4.84 \times 0.0744}{6.016}$$

Sol. $\frac{4.84 \times 0.0744}{6.016} = 0.0598885$

As 4.84 has least number of three significant figures, the result should contain three significant figures only. Hence, the result after rounding off is 0.0599.

ILLUSTRATION 1.5

The density of copper is 7.8 g cm^{-3} and its weight is 5.642 g. Report the volume of copper to correct decimal point.

Sol. $\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{5.642 \text{ g}}{7.8 \text{ g cm}^{-3}} = 0.7233 \text{ cm}^3 = 0.72 \text{ cm}^3$

The result should have two significant figures because the least precise term (7.8) has two significant figures.

ILLUSTRATION 1.6

What is the number of significant figures in Avogadro's number (6.0×10^{23}) and Planck's constant ($6.62 \times 10^{-34} \text{ J s}$).

Sol. Avogadro's number (6.0×10^{23}) has 2 significant figures while Planck's constant ($6.62 \times 10^{-34} \text{ J s}$) has three significant figures since only significant figures of 6.0 and 6.62 are considered.

ILLUSTRATION 1.7

Express the following to four significant figures:

- i. 6.58768×10^5 ii. 8.35783
iii. 98.2350 iv. 0.003586
v. 90000

Sol.

- i. 6.587×10^5 and after rounding off 6.588×10^5 .
ii. 8.357 and after rounding off 8.358.
iii. 98.23 and after rounding off 98.24.

The rightmost digit to be removed is 5, and the preceding number is 3 (odd number), so it is increased by one.

- iv. 0.003586 (zeros after decimal point and to the left of a number are not significant).
v. 9.000×10^4

ILLUSTRATION 1.8

Express the number 68000 in exponential notation which shows

- i. Two significant figures ii. Three significant figures

Sol.

- i. 6.8×10^4 (Two significant figures)
ii. 6.80×10^4 (Three significant figures).

ILLUSTRATION 1.9

An analytic balance has uncertainty in measurement equal to $\pm 1 \text{ mg}$. Then report the result in terms of percentage if the weight of a compound is

- a. 1 g b. 10 g c. 100 g

Sol. a. $1 \pm 0.1\%$ b. $10 \pm 0.01\%$ c. $100 \pm 0.001\%$

The uncertainty in measurement is expressed in terms of percentage by putting \pm sign before it, e.g., $150 \pm 1\%$, etc. Smaller the quantity to be measured, greater is the percentage uncertainty, and the instrument should be more precise for the measurement of smaller quantities.

$$1 \text{ mg} = \frac{1}{1000} \text{ g} = \frac{1}{1000} \times 100 = \frac{1}{10} = 0.1 = 1 \pm 0.1\%$$

Some conversion factors

Table 1.6 From given unit to SI unit

a.	1 amu (or μ) = $1.66053 \times 10^{-27} \text{ kg}$
b. ✓	1 L = 10^{-3} m^3 = 1 dm ³
c.	1 atm = 760 mm or torr = $1.013 \times 10^6 \text{ dynes cm}^{-2}$ = 101325 Pa or N m ⁻²
d.	1 bar = 10^5 N m^{-2} = 10^5 Pa
e.	1 torr or 1 mm = 133.322 Pa or N m ⁻²
f.	1 erg = 10^{-7} J
g.	1 calorie = 4.184 J
h.	1 eV (electron volt) = $1.6022 \times 10^{-19} \text{ J}$
i.	$t^\circ \text{C} = t + 273.15 \text{ K}$
j.	1 Å = 10^{-10} m .

Table 1.7 From given unit to another unit

a.	1 kg = 1000 g
b.	1 g = 1000 mg
c.	1 metric ton = 1000 kg
d.	1 lb = 453.6 g
e.	1 kg = 2.205 lb
f.	1 L = 1000 mL = 1000 cm ³
g.	1 L = 1.056 quarts
h.	1 quart = 0.9463 L
i.	1 mile = 1760 yards
j.	1 yard = 3 feet
k.	1 feet = 12 inches
l.	1 inch = 2.54 cm
m.	1 carat = 3.168 grains
n.	1 g = 15.4 grains

1.5 DIMENSIONAL ANALYSIS

Calculation involving the use of the dimensions of different physical quantities involved is called *dimensional analysis*. The method to convert a physical quantity given in one type of units into some other type of units is called *factor label method* or *unit factor method*. It involves the following steps:

- a. First determine the unit conversion factor/factors. For example, for conversion of inches into centimetres or vice versa,

$$1 \text{ in} = 2.54 \text{ cm}$$

$$\therefore \frac{1 \text{ in}}{2.54 \text{ cm}} = 1 = \frac{2.54 \text{ cm}}{1 \text{ in}}$$

Similarly, for conversion of pounds (lb) into kilogram (kg) or vice versa,

$$1 \text{ kg} = 2.205 \text{ lb}$$

$$\therefore \frac{1 \text{ kg}}{2.205 \text{ lb}} = 1 = \frac{2.205 \text{ lb}}{1 \text{ kg}}$$

Thus quantities such as 2.54 cm per inch or one inch per 2.54 cm and 1 kg per 2.205 lb or 2.205 lb per kg, etc., are called 'unit conversion factor'. If some number is multiplied by these unit factors, i.e., 1, it will not be affected in value.

- b. Multiply the given physical quantity with the unit conversion factor in such manner that gives the desired units, i.e., the numerator should have that part which is required in the desired result.

For example, convert 6 inch into cm. Multiplying the unit conversion factor (containing cm. in the numerator) by 6 to get the desired result.

$$6 \text{ in} = 6 \cancel{\text{ in}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{ in}}} = 15.24 \text{ cm}$$

- c. If the conversion involves various steps, each conversion factor should be used in such a way that the units of the preceding factor cancel out.

Moreover, like other numerical parts, the units can be cancelled, divided, multiplied squared, etc.

ILLUSTRATION 1.10

Convert the following:

- 5 L of a solution into m^3
- 4 days into seconds
- 200 lb into kilogram
- 2.00 km into miles
(1 mile = 1760 yd, 1 yd = 3 ft, 1 in = 2.54 cm)
- 0.800 carat into grams and kilograms
(1 carat = 3.168 grains, and 1 g = 15.4 grains)
- 8.0 km into inches (1 m = 1.094 yards (yd), 1 yd = 36 in)
- 40 Em (exametre) (thickness of Milky way galaxy) into metre
- 1.4 Gm (gigametre) (diameter of sun) into metre
- 41 Pm (petametre) (distance of nearest star) into metre
- 1 fg (femtogram) (mass of human DNA molecule) into kilogram
- 500 Mg (megagram) (mass of a loaded jumbo jet) into kilogram

Sol. a. 1 L = 1000 cm^3 and 1 m = 100 cm which gives

$$\frac{1 \text{ m}}{100 \text{ cm}} = 1 = \frac{100 \text{ cm}}{1 \text{ m}}$$

To get m^3 from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 = \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = (1)^3 = 1$$

$$\text{Now, } 5 \text{ L} = 5 \times 1000 \text{ cm}^3$$

The above is multiplied by the unit factor,

$$5 \times 1000 \cancel{\text{ cm}^3} \times \frac{1 \text{ m}^3}{10^6 \cancel{\text{ cm}^3}} = \frac{5 \text{ m}^3}{10^6} = 5 \times 10^{-3} \text{ m}^3$$

- b. 1 day = 24 hours (h), 1 h = 60 min, and 1 min = 60 s

$$\text{or } \frac{1 \text{ day}}{24 \text{ h}} = 1 = \frac{24 \text{ h}}{1 \text{ day}}$$

$$\text{or } \frac{1 \text{ h}}{60 \text{ min}} = 1 = \frac{60 \text{ min}}{1 \text{ h}}$$

So, 4 days = = seconds

The unit factors can be multiplied in series in one step only as follows:

$$4 \cancel{\text{ days}} \times \frac{24 \cancel{\text{ h}}}{1 \cancel{\text{ day}}} \times \frac{60 \cancel{\text{ min}}}{1 \cancel{\text{ h}}} \times \frac{60 \text{ s}}{1 \cancel{\text{ min}}} = 4 \times 24 \times 60 \times 60 \text{ s} = 345600 \text{ s}$$

- c. 1 kg = 2.205 lb

$$\therefore \frac{2.205 \text{ lb}}{1 \text{ kg}} = 1 = \frac{1 \text{ kg}}{2.205 \text{ lb}}$$

$$\text{Hence, } 200 \text{ lb} = 200 \cancel{\text{ lb}} \times \frac{1 \text{ kg}}{2.205 \cancel{\text{ lb}}} = 90.7 \text{ kg}$$

- d. 1 km = 1000 m, 1 m = 100 cm, 1 in = 2.54 cm
1 ft = 12 in, 1 yd = 3 ft, 1 mile = 1760 yd

$$\begin{aligned} \therefore 2.00 \text{ km} &= 2.00 \cancel{\text{ km}} \times \frac{1000 \cancel{\text{ m}}}{1 \cancel{\text{ km}}} \times \frac{100 \cancel{\text{ cm}}}{1 \cancel{\text{ m}}} \\ &\times \frac{1 \cancel{\text{ in}}}{2.54 \cancel{\text{ cm}}} \times \frac{1 \cancel{\text{ ft}}}{12 \cancel{\text{ in}}} \times \frac{1 \cancel{\text{ yd}}}{3 \cancel{\text{ ft}}} \times \frac{1 \text{ mile}}{1760 \cancel{\text{ yd}}} \\ &= \frac{2.00 \times 1000 \times 100}{2.54 \times 12 \times 3 \times 1760} = 1.2427 \\ &= 1.24 \text{ miles} \end{aligned}$$

But the result is to be reported upto three significant figures since the least precise term (2.00) has three significant figures.

- e. $\frac{1 \text{ carat}}{3.168 \text{ grains}} = 1 = \frac{3.168 \text{ grains}}{1 \text{ carat}}$
and $\frac{1 \text{ g}}{15.4 \text{ grains}} = 1 = \frac{15.4 \text{ grains}}{1 \text{ g}}$

$$0.800 \text{ carat} = 0.800 \cancel{\text{carat}} \times \frac{3.168 \text{ grains}}{1 \cancel{\text{carat}}} \times \frac{1 \text{ g}}{15.4 \text{ grains}}$$

$$= \frac{0.800 \times 3.168 \times 1}{15.4} = 0.16 \text{ g}$$

$$0.16 \text{ g} = 0.16 \cancel{\text{g}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 0.0001 \text{ kg}$$

f. The unit conversion factors are:

$$\frac{1000 \text{ m}}{1 \text{ km}} = 1 = \frac{1 \text{ km}}{1000 \text{ m}}$$

$$\text{and } \frac{1.094 \text{ yd}}{1 \text{ m}} = 1 = \frac{1 \text{ m}}{1.094 \text{ yd}}$$

$$\text{and } \frac{36 \text{ in}}{1 \text{ yd}} = 1 = \frac{1 \text{ yd}}{36 \text{ in}}$$

$$\text{Thus, } 8.0 \text{ km} = 8.0 \cancel{\text{km}} \times \frac{1000 \cancel{\text{m}}}{1 \cancel{\text{km}}} \times \frac{1.094 \cancel{\text{yd}}}{1 \cancel{\text{m}}} \times \frac{36 \cancel{\text{in}}}{1 \cancel{\text{yd}}}$$

$$= 315072 = 3.1 \times 10^5 \text{ in}$$

The result is to be reported upto 2 significant figures since the least precise term (8.0) has 2 significant figures.

g. 1 Em (exametre) = 10^8 m

$$\therefore 40 \text{ Em} = 40 \cancel{\text{Em}} \times \frac{10^{18} \text{ m}}{1 \cancel{\text{Em}}} = 4 \times 10^{19} \text{ m}$$

h. 1 Gm (gigametre) = 10^9 m

$$\therefore 1.4 \text{ Gm} = 1.4 \times \cancel{\text{Gm}} \times \frac{10^9 \text{ m}}{1 \cancel{\text{Gm}}} = 1.4 \times 10^9 \text{ m}$$

i. 1 Pm (petametre) = 10^{15} m

$$\therefore 41 \text{ Pm} = 41 \times \cancel{\text{Pm}} \times \frac{10^{15} \text{ m}}{1 \cancel{\text{Pm}}} = 41 \times 10^{15} \text{ m}$$

j. 1 fg (femtogram) = 10^{-15} g and $1 \text{ kg} = 1000 \text{ g}$

$$\therefore 1 \text{ fg (femtogram)} = 1 \cancel{\text{fg}} \times \frac{10^{-15} \cancel{\text{g}}}{1 \cancel{\text{fg}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}}$$

$$= 10^{-18} \text{ kg}$$

k. 1 Mg (Megagram) = 10^6 g and $1 \text{ kg} = 1000 \text{ g}$

$$\therefore 500 \text{ Mg} = 500 \cancel{\text{Mg}} \times \frac{10^6 \cancel{\text{g}}}{1 \cancel{\text{Mg}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}}$$

$$= 5 \times 10^5 \text{ kg}$$

e. 2.53 mm

f. 7.85 mL

g. 0.0528 in

h. 52 μg

i. 5 days

j. 5 L

k. 14 lb in^{-2} (atmospheric pressure)

l. 6.86 g cm^{-3} (density of a metal)

Sol. a. SI unit of length is metre.

$$1 \text{ ft} = 12 \text{ in}$$

$$\therefore 6' 10'' = 12 \times 6 + 10 = 82'' \text{ or } 82 \text{ in}$$

$$\therefore 82 \text{ in} = 82 \cancel{\text{in}} \times \frac{2.54 \cancel{\text{cm}}}{1 \cancel{\text{in}}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}}$$

$$= 2.0828 \text{ m} = 2.08 \text{ m}$$

b. SI unit of mass is kg.

$$1 \text{ lb} = 454 \text{ g}$$

$$\therefore 200 \text{ lb} = 200 \cancel{\text{lb}} \times \frac{454 \cancel{\text{g}}}{1 \cancel{\text{lb}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 90.8 \text{ kg}$$

c. SI unit of speed is m s^{-1} .

$$\frac{60 \text{ miles}}{1 \text{ hour}} = \frac{60 \cancel{\text{miles}}}{3600 \text{ s}} \times \frac{1760 \cancel{\text{yd}}}{1 \cancel{\text{mile}}} \times \frac{3 \cancel{\text{ft}}}{1 \cancel{\text{yd}}} \times \frac{12 \cancel{\text{in}}}{1 \cancel{\text{ft}}} \times \frac{2.54 \cancel{\text{cm}}}{1 \cancel{\text{in}}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}}$$

$$= 26.82 \text{ m s}^{-1} = 26.8 \text{ m s}^{-1}$$

d. SI unit of temperature is Kelvin

$$-20^\circ\text{C} = -20 + 273.15 \text{ K} = 253.15 \text{ K}$$

e. SI unit of length is metre (m).

$$1 \text{ m} = 100 \text{ cm}, 1 \text{ cm} = 10 \text{ mm}$$

Unit conversion factors are:

$$\therefore \frac{1 \text{ m}}{100 \text{ cm}} = 1 = \frac{100 \text{ cm}}{1 \text{ m}}$$

$$\text{and } \frac{1 \text{ cm}}{10 \text{ mm}} = 1 = \frac{10 \text{ mm}}{1 \text{ cm}}$$

$$\therefore 2.53 \text{ mm} = 2.53 \cancel{\text{mm}} \times \frac{1 \cancel{\text{cm}}}{10 \cancel{\text{mm}}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}}$$

$$= 2.53 \times 10^{-3} \text{ m}$$

f. SI unit of volume is $(\text{metre})^3$ or m^3 .

$$7.85 \text{ mL} = 7.85 \cancel{\text{mL}} \times \frac{1 \cancel{\text{cm}^3}}{10 \cancel{\text{mL}}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}}$$

$$= 7.85 \times 10^{-6} \text{ m}^3$$

g. SI unit of length is metre (m).

$$0.0528 \text{ in} = 0.0528 \cancel{\text{in}} \times \frac{2.54 \cancel{\text{cm}}}{1 \cancel{\text{in}}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}}$$

$$1.341 \times 10^{-3} \text{ m}$$

ILLUSTRATION 1.11

Express the following in SI units:

a. $6'10''$

b. 200 lb

c. 60 miles h^{-1}

d. -20°C

h. SI unit of mass is kg.

and $1 \mu\text{g}$ (micro gram) = 10^{-6} g

$$52 \mu\text{g} = 52 \cancel{\mu\text{g}} \times \frac{10^{-6} \cancel{\text{g}}}{1 \cancel{\mu\text{g}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 5.2 \times 10^{-8} \text{ kg}$$

i. SI unit of time is second (s).

$$\therefore 5 \text{ days} = 5 \cancel{\text{days}} \times \frac{24 \cancel{\text{h}}}{1 \cancel{\text{day}}} \times \frac{60 \cancel{\text{min}}}{1 \cancel{\text{h}}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} \\ = 5 \times 24 \times 60 \times 60 \text{ s} = 432000 \text{ s}$$

j. SI unit of volume is dm^3 .

$$\therefore 5 \text{ L} = 5 \cancel{\text{L}} \times \frac{1000 \cancel{\text{cm}^3}}{1 \cancel{\text{L}}} \times \frac{1 \text{ dm}}{10 \cancel{\text{cm}}} \times \frac{1 \text{ dm}}{10 \cancel{\text{cm}}} \times \frac{1 \text{ dm}}{10 \cancel{\text{cm}}} \\ = 5 \text{ dm}^3$$

k. SI unit of pressure is kg m^{-2} and $1 \text{ kg} = 2.205 \text{ lb}$.

$$\therefore \frac{14 \text{ lb}}{1 \text{ in}^2} = \frac{14 \cancel{\text{lb}}}{1 \cancel{\text{in}^2}} \times \frac{1 \text{ kg}}{2.205 \cancel{\text{lb}}} \times \frac{1 \cancel{\text{in}}}{2.54 \cancel{\text{cm}}} \\ \times \frac{1 \cancel{\text{in}}}{2.54 \cancel{\text{cm}}} \times \frac{100 \cancel{\text{cm}}}{1 \text{ m}} \times \frac{100 \cancel{\text{cm}}}{1 \text{ m}} \\ = \frac{14 \times 100 \times 100}{2.205 \times 2.54 \times 2.54} \\ = 9841.28 \text{ kg m}^{-2} \\ = 9841.3 \text{ kg m}^{-2} \text{ (rounding off)}$$

l. SI unit of density is kg m^{-3} .

$$\frac{6.86 \text{ g}}{1 \text{ cm}^3} = \frac{6.86 \cancel{\text{g}}}{1 \cancel{\text{cm}^3}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} \times \frac{100 \cancel{\text{cm}}}{1 \text{ m}} \\ \times \frac{100 \cancel{\text{cm}}}{1 \text{ m}} \times \frac{100 \cancel{\text{cm}}}{1 \text{ m}} \\ = \frac{6.86 \times 10^6}{10^3} = 6860 \text{ kg m}^{-3}$$

1.6 LAWS OF CHEMICAL COMBINATION

The study of chemical reactions is governed by five basic laws. These are:

- Law of conservation of mass
- Law of constant composition or law of definite proportions
- Law of multiple proportions
- Law of equivalent, reciprocal, or combining proportions or weights
- Gay Lussac's law of gaseous volumes

The first four laws are related with mass whereas the fifth law is related with the volume of reacting gases.

1.6.1 LAW OF CONSERVATION OF MASS

This law was studied by French chemist *Antonie Lavoisier* in 1789.

It states that during the course of chemical processes, matter is neither created nor destroyed. For example, if masses m and n of substances A and B react to form masses x and y of substances C and D, respectively, then

$$m + n = x + y$$

It follows that the total mass of reactants is equal to the total mass of products.

ILLUSTRATION 1.12

Five grams of KClO_3 yield 3.041 g of KCl and 1.36 L of oxygen at standard temperature and pressure. Show that these figures support the law of conservation of mass within limits of $\pm 0.4\%$ error.

Sol. According to gram-molecular volume law, 22.4 L of all gases and vapours at STP weigh equal to their molecular weights denoted in grams.

$$\therefore \text{Weight of 1.36 L of oxygen at STP} = \frac{32 \times 1.36}{22.4} = 1.943 \text{ g}$$

Weight of KCl formed = 3.041 g (given)

$$\therefore \text{Total weight of product (KCl + O}_2\text{)} \\ = 3.041 + 1.943 = 4.984 \text{ g}$$

$$\text{Error} = 5 - 4.984 = 0.016 \text{ g}$$

$$\therefore \% \text{ error} = \frac{0.016 \times 100}{5} = 0.32$$

Hence, the law of conservation of mass is valid within limits of -0.4% error. Thus, the law is supported.

ILLUSTRATION 1.13

0.22 g of a hydrocarbon (i.e., a compound containing carbon and hydrogen only) on complete combustion with oxygen gave 0.9 g water and 0.44 g carbon dioxide. Show that these results are in accordance with the law of conservation of mass (atomic mass of C = 12, H = 1, O = 16).

Sol. Carbon and hydrogen in the hydrocarbon on combustion form carbon dioxide and water. From the formulae of CO_2 and H_2O , the weights of carbon and hydrogen contained in 0.44 g CO_2 and 0.9 g water, respectively, can be calculated as under:

$$\text{Molecular weight of CO}_2 = 12 + 32 = 44$$

$$\text{Molecular weight of H}_2\text{O} = 2 + 16 = 18$$

$$\text{Weight of carbon in 0.44 g of CO}_2 = \frac{12 \times 0.44}{44} = 0.12 \text{ g}$$

$$\text{Weight of hydrogen in 0.9 g of H}_2\text{O} = 2 \times \frac{0.9}{18} = 0.10 \text{ g}$$

$$\text{Total weight of C and H in the hydrocarbon after combustion} \\ = 0.12 + 0.10 = 0.22 \text{ g}$$

Since the weight of carbon and hydrogen after combustion is the same as the weight of hydrocarbon (containing carbon and hydrogen only) after combustion, the results are in accordance with the law of conservation of mass.

1.6.2 LAW OF CONSTANT OR DEFINITE COMPOSITION OR PROPORTIONS

This law was studied by French chemist *Joseph Proust* (1799).

It states that the same compound is always composed of the same elements combined together in the same or fixed proportions by weight.

Thus, if hydrogen and oxygen unite to form water, no matter in whatever way and at whichever place it is produced, it is always

composed of these elements combined together in the same proportion by weight. So, chemical compounds have always a definite composition by weight.

Note: Law of constant composition is not true for all types of compounds but true only for the compounds obtained from one isotope. For example, three isotopes of carbon are C^{12} , C^{13} , and C^{14} ; when it forms CO_2 from C^{12} , the ratio of masses is $12 : 32 = 3 : 8$. But from C^{13} and C^{14} the ratio are $13 : 22$ and $14 : 32 (= 7 : 16)$, which is not same as in the first case.

ILLUSTRATION 1.14

0.7 g of iron reacts directly with 0.4 g of sulphur to form ferrous sulphide. If 2.8 g of iron is dissolved in dilute HCl and excess of sodium sulphide solution is added, 4.4 g of iron sulphide is precipitated. Prove the law of constant composition.

Sol. The ratio of the weights of iron and sulphur in the first sample of the compound is $Fe : S :: 0.7 : 0.4$ or $7 : 4$.

According to the second experiment, 2.8 g of iron gives 4.4 g ferrous sulphide, or 2.8 g Fe combines with $S = 4.4 - 2.8$
 $= 1.6$ g

Therefore, the ratio of the weights of $Fe : S :: 2.8 : 1.6$ or $7 : 4$.

Since the ratio of the weights of the two elements is same in both the cases, the law of constant composition is true.

ILLUSTRATION 1.15

1.375 g of cupric oxide was reduced by heating in a current of hydrogen and the weight of copper that remained was 1.098 g. In another experiment, 1.179 g of copper was dissolved in nitric acid and the resulting copper nitrate converted into cupric oxide by ignition. The weight of cupric oxide formed was 1.476 g. Show that these result illustrate the law of constant composition.

Sol. First case:

Copper oxide taken = 1.375 g

Copper left = 1.098 g

\therefore Oxygen present = $1.375 \text{ g} - 1.098 = 0.277 \text{ g}$

Hence, % of O in $CuO = \frac{0.277 \times 100}{1.375} = 20.14$

Second case:

Copper taken = 1.179 g

Copper oxide formed = 1.476 g

\therefore Oxygen present = $1.476 \text{ g} - 1.179 = 0.297 \text{ g}$

Hence, % of O in $CuO = \frac{0.297 \times 100}{1.476} = 20.12$

Hence, percentage of oxygen is same in both of the above cases, so the law is proved.

ILLUSTRATION 1.16

112 mL of hydrogen combines with 56 mL of oxygen to form water. When 224 mL of hydrogen is passed over heated cupric oxide, the cupric oxide loses 0.160 g of its weight. All volumes are measured at STP. Show that the result agrees with the law of constant composition (22.4 L of hydrogen and oxygen at STP weigh, respectively, 2 g and 32 g).

Sol. First case:

Weight of 112 mL of H_2 at STP = $\frac{112 \times 2}{22400} = 0.01 \text{ g}$

Weight of 56 mL of O_2 at STP = $\frac{56 \times 32}{22400} = 0.08 \text{ g}$

Second case:

Weight of 224 mL of H_2 at STP = $\frac{224 \times 2}{22400} = 0.02 \text{ g}$

Weight of oxygen taken away from cupric oxide by 224 mL or 0.02 g of H_2 at STP = 0.160 g

Weight of oxygen that combines with 0.01 g of H_2 in the second case = $\frac{0.160 \times 0.01}{0.02} = 0.08 \text{ g}$

Thus, the two weights of oxygen that combine with the same weight of hydrogen are same in the two cases. Hence, the law of constant composition is proved.

1.6.3 LAW OF MULTIPLE PROPORTIONS

This law was studied by John Dalton (1803).

It states that if two elements combine together to form several compounds, then the weight of one of these elements, which combines with a fixed weight of the other, are in ratio of simple whole numbers.

For example, sulphur combines with oxygen to form SO_2 and SO_3 . According to the law, the weights of oxygen that should combine with a fixed weight of sulphur, say 32 parts, should be in a simple whole number ratio to each other. Actually, in SO_2 and SO_3 , the weights of oxygen that combine with 32 parts (atomic weight) of sulphur are in the ratio of $32 : 48$ or $2 : 3$. Similarly, carbon combines with oxygen to form carbon monoxide (CO) and carbon dioxide (CO_2). The weights of oxygen that combine with 12 parts by weight of carbon in the two compounds are in the respective ratio of $16 : 32$ or $1 : 2$. Thus, the law is true. Similarly, if the weights of carbon that combine with the same weight of oxygen, say 16 parts, be calculated in the compounds, carbon monoxide and carbon dioxide, they will be in the ratio of $12 : 6$ or $2 : 1$. The ratio being simple, the law is equally true in this way.

ILLUSTRATION 1.17

Elements X and Y form two different compounds. In the first compound, 0.324 g X is combined with 0.471 g Y . In the second compound, 0.117 g X is combined with 0.509 g Y . Show that these data illustrate the law of multiple proportions.

Sol. In the first compound:

0.324 g of X combines with 0.471 g of Y .

In the second compound:

0.117 g of X combines with 0.509 g of Y .

Therefore, 0.324 g of X combines with the weight of Y

$$= \frac{0.509 \times 0.324}{0.117} = 1.4095 \text{ g}$$

Now, the weights of Y that combine with the same weight of X , i.e., 0.324 g of it, are in the ratio of $0.471 : 1.4095$ or $1 : 3$. The ratio, being simple, illustrates the law of multiple proportions.

ILLUSTRATION 1.18

An element forms two oxides of 2.900 g and 2.250 g of these oxides each was found to contain 1.12 L of O_2 at STP. Which law of chemical combination is illustrated by these data?

Sol. According to gram molecular volume law, 22.4 L of all gases at STP weigh equal to their molecular weights denoted in grams. Hence, the weight of 1.12 L of oxygen at STP

$$= \frac{32 \times 1.12}{22.4} = 1.600 \text{ g}$$

In the first oxide:

Weight of oxide = 2.900 g; weight of O = 1.600 g

\therefore Weight of the element = 2.900 – 1.600 = 1.300 g

In the other oxide:

Weight of oxide = 2.250 g; weight of O = 1.600 g

Weight of element = 2.250 – 1.600 = 0.650 g

Thus, the weights of the element that combine with the same weight of oxygen in its two oxides are in the ratio of 1.3 : 0.65 or 2 : 1 a simple ratio. Hence, it illustrates the law of multiple proportions.

ILLUSTRATION 1.19

Carbon combines with hydrogen to form three compounds A, B, and C. The percentage of hydrogen in A, B, and C is 25, 14.3, and 7.7, respectively. (a) Find the empirical formulae of the compounds. (b) Which law of chemical combination does this example illustrate? How?

Sol.

a. Element	A	B	C
Carbon	75%	85.7%	92.3%
Hydrogen	25%	14.3%	7.7%
Atomic ratios:			
Carbon : Hydrogen	$\frac{75}{12} : \frac{25}{1}$	$\frac{85.7}{12} : \frac{14.3}{1}$	$\frac{92.3}{12} : \frac{7.7}{1}$
or	6.25 : 25	7.14 : 14.3	7.7 : 7.7
or	1 : 4	1 : 2	1 : 1
Empirical formulae	CH_4	CH_2	CH

- b. Since the number of H atoms or the weights of H that combine with one atom or 12 parts by weight of carbon in the three cases bear a simple ratio of 4 : 2 : 1, hence, the law of multiple proportions is illustrated.

ILLUSTRATION 1.20

Two oxides of a metal contain 27.6% and 30.0% of Oxygen, respectively. If the formula of the first be M_3O_4 . Find that of the second.

Sol. First oxide

Oxygen = 27.6%

Metal = 72.4%

Formula = M_3O_4

Let the atomic weight the metal be x .

Second oxide

Oxygen = 30.0%

Metal = 70.0%

Formula = ?

Therefore, percentage by weight of the metal in the compound M_3O_4

$$= \frac{3 \times x \times 100}{3x + 64} = 72.4 \text{ (given)}$$

Hence, $x = 55.97 \approx 56$.

Thus, having known the atomic weights of the metal and oxygen, empirical formula of the second oxide can be worked out as under:

Element	%	Atomic ratio	Least ratio	Whole number ratio
Oxygen	30.00	$\frac{30.00}{16} = 1.88$	$\frac{1.88}{1.25} = 1.5$	3
Metal	70.00	$\frac{70.00}{56} = 1.25$	$\frac{1.25}{1.25} = 1$	2

Thus, the formula of the second oxide is M_2O_3 .

ILLUSTRATION 1.21

If the masses of Mn and O are in the ratio of 55 : 16 in MnO , what is the ratio of O that combines with the same mass of Mn in MnO_2 and Mn_2O_7 ?

Sol. In MnO , 1 atom of Mn combines with 1 atom of O (16).

Therefore, in MnO_2 , 1 atom of Mn will combine with $16 \times 2 = 32$ parts of O. Again 2 atoms of Mn combine with 7 atoms or $7 \times 16 = 112$ parts of O in Mn_2O_7 . Hence, 1 atom of Mn will combine with $112/2 = 56$ parts of oxygen. The ratio of O that combines with the same mass of Mn is $MnO_2 : Mn_2O_7 :: 32 : 56$, i.e., 4 : 7.

1.6.4 LAW OF EQUIVALENT, RECIPROCAL, OR COMBINING PROPORTIONS OR WEIGHTS

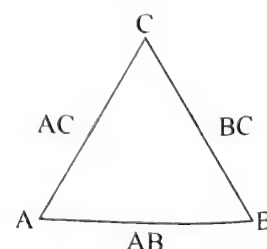
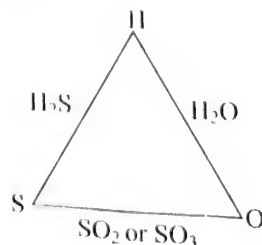
This law was studied by Richter (1792).

It states that if two elements A and B combine with a fixed mass of element C to form two compounds, then the ratio of A and B in these compounds is same or simple multiple of the ratio when they combine with each other.

The weights of the elements that combine with a constant weight of a standard substance (say, hydrogen, oxygen, or chlorine) are called their equivalent or combining weights. Also, according to the law, substances react together in the ratio of their combining or equivalent weights or their multiples or sub-multiples. Reverse of the law of reciprocal proportions is thus the law of equivalent proportions.

In simple words, the law of equivalent proportions may be defined as under:

Substances react together in the ratio of their equivalent weight.



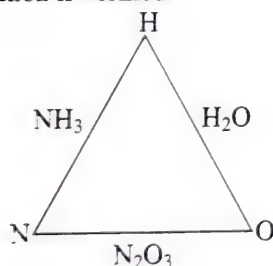
This law is also defined as under :

If two elements A and B combine with another element C, they will combine with one another in the same ratio or a multiple or sub-multiple of the ratio in which they combine with constant or fixed weight of C.

The law may be explained as under: sulphur and oxygen combine with hydrogen to form sulphuretted hydrogen and water. The weights of S and O that combine with the same weight of H (say, 2 parts) in these two cases are 32 parts and 16 parts, respectively. Now, according to the law, if S and O were to combine with each other, they will do so in the ratio of 32 : 16, i.e., 2 : 1 or a multiple or a sub-multiple of this ratio. In SO_2 , 32 parts of S combine with 32 parts of O, the ratio is 32 : 32 or 1 : 1. This latter ratio, i.e., 1 : 1 is related with the ratio of S and O, that combines with the same weight of hydrogen, as determined above, i.e., (2 : 1) as 1 : 2. Similarly, in SO_3 , 32 parts of S combine with 48 parts of oxygen, the ratio of S : O is 32 : 48 or 2 : 3, is also related to the ratio (2 : 1) as three times this ratio. The ratio, i.e. (2 : 3), in SO_3 , is also related to the ratio (1 : 1) in SO_2 as 2 : 3. Thus, these ratios are simple sub-multiples, viz., 1/2 and 1/3, of the first ratio, and this is in accordance with the law. Examples that follow will illustrate the above points still further.

ILLUSTRATION 1.22

Ammonia contains 82.35% of nitrogen and 17.65% of hydrogen. Water contains 88.90% of oxygen and 11.10% of hydrogen. Nitrogen trioxide contains 63.15% of oxygen and 36.85% of Nitrogen. Show by calculations from these data which law of chemical combination is verified.



Sol.

a. Ammonia contains

N = 82.35 parts, H = 17.65 parts

Now, the weight of nitrogen that combines with 1 part by

$$\text{weight of H in } \text{NH}_3 = \frac{82.35}{17.65} = 4.67$$

b. Water contains

H = 11.10 parts, O = 88.90 parts

Weight of oxygen that combines with 1 part by weight

$$\text{of H in } \text{H}_2\text{O} = \frac{88.90}{11.10} = 8.01$$

In the two compounds NH_3 and H_2O , weights of nitrogen and oxygen that combine with the same weight, i.e., 1 part by weight of hydrogen, are in the ratio of 4.67 : 8.01 or 1 : 1.71 (ratio I).

c. Nitrogen trioxide contains

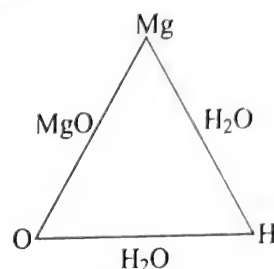
N = 36.85, O = 63.15

In this compound, the ratio of the weights of nitrogen to oxygen is 36.85 : 63.15 or 1 : 1.71 (ratio II).

Ratios (I) and (II) being the same, these data illustrate the validity of the law of reciprocal proportion.

ILLUSTRATION 1.23

Show that the results given below taken together illustrate a law of chemical action: (a) 0.46 g of magnesium produces 0.77 g of magnesium oxide, (b) 0.82 g of magnesium liberates 760 mL of hydrogen at STP from an acid (weight of 1 mL of hydrogen at STP = 0.00009 g), and (c) 1.25 g of water results from the union of 1.11 g of oxygen and hydrogen.



Sol.

a. Magnesium oxide contains

$$\text{Mg} = 0.46 \text{ g, O} = 0.77 - 0.46 = 0.31 \text{ g}$$

Therefore, weight of oxygen that combines with 1 g of

$$\text{Mg} = \frac{0.31}{0.46} = 0.674 \text{ g}$$

b. 0.82 g of Mg liberates $\text{H}_2 = 0.00009 \times 760 = 0.068 \text{ g}$

Thus, the weight of H_2 that will be liberated by 1 g of

$$\text{Mg} = \frac{0.068}{0.82} = 0.083 \text{ g}$$

According to (a) and (b), the ratio of the weights of O : H that combine with or is displaced by the same weight of magnesium is 0.674 : 0.083 or 8 : 1.

Again, according to (c), 1.25 g of water contains O = 1.11 g and H = 1.25 - 1.11 = 0.14 g

Therefore, The ratio of O : H :: 1.11 : 0.14 or 8 : 1

Hence, the ratio being the same, the law of reciprocal proportions is illustrated.

ILLUSTRATION 1.24

Aluminium oxide contains 52.9% aluminium and carbon dioxide contains 27.27% carbon. Assuming the law of reciprocal proportions, calculate the percentage of aluminium in aluminium carbide.

Sol. Aluminium oxide contains: Al = 52.9 parts; O = 47.1 parts
Carbon dioxide contains: C = 27.27 parts; O = 72.73 parts

According to the law of reciprocal proportions, the weights of Al and C that would combine with each other to form aluminium carbide would either be the same or simple multiple of their weights that combine with the same weight of oxygen in aluminium oxide and carbon dioxide.

Hence, the weight of carbon that would combine with 47.1 g of oxygen in $\text{CO}_2 = \frac{27.27 \times 47.1}{72.73} = 17.62$, as also, in aluminium oxide, 52.9 g of Al combine with 47.1 g of oxygen.

Thus, aluminium and carbon should be present in aluminium carbide in the ratio of 52.9 : 17.62, i.e., 3 : 1 or a simple multiple of this ratio. Hence, in aluminium carbide, percent of Al = $\frac{52.9 \times 100}{70.52} = 75.01$.

1.6.5 GAY LUSSAC'S LAW OF GASEOUS VOLUMES

This law was studied by Gay Lussac in 1808.

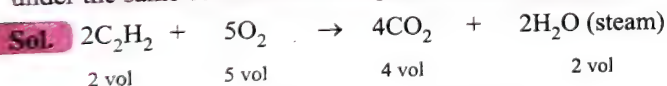
It states that when gases react together, they do so in volumes which bear a simple ratio to one another and also to the volumes of the products, if gaseous, all measurements being made under similar conditions of temperature and pressure.

It is found by experiments that when hydrogen and chlorine combine together to form hydrochloric acid gas, equal volumes of H_2 and Cl_2 combine to produce double the volume of HCl gas under ordinary conditions. Thus, 1 volume of H_2 combines with 1 volume of Cl_2 to form 2 volumes of HCl gas, i.e., their ratio, by volume, viz., 1 : 1 : 2, is simple and that is in accordance with the law. Similarly, it is found that 2 volumes of carbon monoxide combine with 1 volume of oxygen to form 2 volumes of carbon dioxide. Their ratio by volume, viz., 2 : 1 : 2, is also simple and is in accordance with the law.

With the help of equations and the application of Avogadro's hypothesis, problems involving volumes can be solved.

ILLUSTRATION 1.25

Air contains 21% oxygen by volume. Calculate the theoretical volume of air which will be required for burning completely 500 cubic ft of acetylene gas (C_2H_2). All volumes are measured under the same conditions of temperature and pressure.



(Here, the ratio of the reacting molecules and those of the products is taken as the ratio of their volumes. This is in accordance with Avogadro's hypothesis—equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules or its reverse, namely, equal number of molecules under similar conditions of temperature and pressure occupy equal volumes, is equally true). The ratio by volumes of reactants and products is apparently simple.

According to the above equation:

2 volumes of acetylene require 5 volumes of O_2 for combustion.

\therefore 500 cu. ft. of acetylene will require O_2

$$= \frac{5 \times 500}{2} = 1250 \text{ cu. ft.}$$

Hence, the quantity of air required

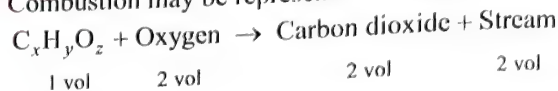
$$= \frac{100 \times 1250}{21} = 5952.38 \text{ cu. ft.}$$

ILLUSTRATION 1.26

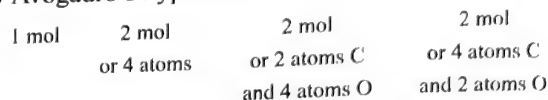
One volume of a gaseous compound containing carbon, hydrogen, and oxygen was burnt in the presence of 2 volumes of oxygen. The resultant gases contained 2 volumes of carbon dioxide and 2 volumes of steam. Find the molecular formula of the compound, if all the volumes were measured under the same conditions of temperature and pressure.

Sol. Let the formula of the compound be $\text{C}_x\text{H}_y\text{O}_z$.

Combustion may be represented as under:



By Avogadro's hypothesis:



Now, 2 molecules of CO_2 contain 2 atoms of carbon and these must have come from the compound. Hence, value of $x = 2$. Again, 2 molecules of steam contain 4 atoms of hydrogen and they, too, have come from the compound. Hence, the value of $y = 4$.

By the comparison of oxygen atoms on both sides of the above equation, the value of z works out to be 2.

Hence, the molecular formula of the compound is $\text{C}_2\text{H}_4\text{O}_2$.

1.7 DALTON'S ATOMIC THEORY

Matter is composed of small indivisible particles called 'a-tomio' (meaning indivisible) (given by Democritus, a Greek Philosopher, 460–370 BC).

However, to describe the structure of matter which could explain the experimental facts about elements, compounds, and mixtures and also the laws of chemical combinations, John Dalton, in 1808, published 'A New System of Chemical Philosophy' in which he proposed the following concepts:

- Matter consists of very small indivisible particles called atoms.
- All the atoms of same elements have identical properties including size, mass, and shapes.
- Atoms of different elements have different masses and also have different chemical properties.
- When atoms of same or different elements combine together to form compounds, they combine in a fixed ratio, a simple whole number ratios, such as 1 : 1, 1 : 2, 2 : 1, 2 : 3, etc.
- Atoms of two elements may combine in different ratios to form more than one compound, e.g., carbon combines with oxygen to form CO and CO_2 in 1:1 and 1:2 ratios, respectively. Similarly, sulphur combines with oxygen to form SO_2 and SO_3 in 1:2 and 1:3 ratios, respectively.
- Atoms in a chemical reactions are neither created nor destroyed but they get reorganised.
- An atom is the smallest particle which takes part in a chemical reaction, i.e., fractions of atom do not take part in a chemical reaction.

Dalton's theory could explain the laws of chemical combination.

1.7.1 EXPLANATION OF THE LAWS OF CHEMICAL COMBINATIONS BY DALTON'S THEORY

- Law of conservation of mass: Matter consists of atoms (postulate a) and can neither be created nor destroyed (postulate f). Hence, matter can neither be created nor destroyed.
- Law of constant composition: Postulates (d) and (e) explain this law.
- Law of multiple proportions: Postulate (e) explains this law.
- Law of reciprocal proportions: Since atoms combine with each other in simple ratio (postulate e), therefore, ratio of all the atoms involved is simple or some simple multiple of each other.

1.7.2 LIMITATIONS OF DALTON'S ATOMIC THEORY

The main limitations of Dalton's atomic theory are:

- It explains the law of chemical combination by mass but does not explain the law of gaseous volumes.
- It does not explain why atoms of same or different elements combine to form molecules.
- It does not explain why atoms of different elements have different masses, sizes, valencies, etc.
- It does not distinguish between the ultimate particles of an element or a compound.
- It does not explain the nature of binding force between the atoms of molecules responsible for the existence of matter in solids, liquids, and gases.

1.8 ATOMIC MASS

The mass of an atom or the atomic mass is very small since atoms are extremely small. In the 19th century, scientists could determine the mass of one atom relative to another by experimental means. The atomic masses of all the elements were obtained by comparing with mass of lightest element, i.e., hydrogen taken as 1 (without any units).

Presently, mass spectroscopy is used for determining the atomic masses very accurately. However, the present system of atomic masses is based on carbon-12 (^{12}C), an isotope of carbon, as the standard and has been agreed upon in 1961.

^{12}C is assigned a mass of exactly 12 atomic mass unit (amu) and masses of all other atoms are given relative to this standard.

One *atomic mass unit* is defined as mass exactly equal to $1/12$ th the mass of one carbon-12 atom.

$$\therefore 1 \text{ amu} = \frac{12}{12 \times 6.022 \times 10^{23}} = 1.66056 \times 10^{-24} \text{ g}$$

$$= 1.66056 \times 10^{-27} \text{ kg}$$

$$\text{Mass of an atom of hydrogen} = 1.6736 \times 10^{-24} \text{ g}$$

$$\text{Mass of H-atom in amu} = \frac{1.6736 \times 10^{-24} \text{ g}}{1.66056 \times 10^{-24} \text{ g}}$$

$$= 1.0078 \text{ amu} = 1.008 \text{ amu}$$

$$\text{Mass of oxygen-16 } (^{16}\text{O}) \text{ in amu} = 15.995 \text{ amu}$$

Presently, 'amu' has been replaced by 'u' known as *unified mass*.

1.8.1 Average Atomic Mass

In calculating the atomic masses of elements, average atomic masses of elements are taken. Various naturally occurring elements have more than one isotope. The average atomic mass of an element is determined by taking into account the existence of these isotopes and their relative percent occurrence. For example, the average atomic mass of carbon is calculated from the data given below:

Isotope	Relative abundance	Atomic mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2×10^{-10}	14.00317

Average atomic mass of carbon

$$= (0.98892)(12 \text{ u}) + (0.01108)(13.00335 \text{ u})$$

$$+ (2 \times 10^{-12})(14.00317 \text{ u})$$

$$= 12.011 \text{ u}$$

Chlorine is a mixture of two isotopes with atomic masses 35u and 37u and they are present in the ratio of 3:1.

$$\text{Therefore, average atomic mass of Cl} = \frac{35 \times 3 + 37 \times 1}{3 + 1} = 35.5 \text{ u}$$

Similarly, the average atomic masses of other elements can be calculated.

1.8.2 GRAM ATOMIC MASS

The atomic mass of an element expressed in grams is called Gram atomic mass. It is also called *one gram atom*.

Atomic mass of sodium = 23 amu

Gram atomic mass or one gram atom of sodium = 23 g

Atomic mass of oxygen = 16 amu

Gram atomic mass or one gram atom of oxygen = 16 g

1.8.3 MOLECULAR MASS

Molecular mass is the sum of atomic masses of elements multiplied by the atomic mass of each element by the number of its atoms present in a molecule. For example:

$$\text{Molecular mass of ethane } (\text{C}_2\text{H}_6) = 2(12.011 \text{ u}) + 6(1.008 \text{ u})$$

$$= 30.07 \text{ u}$$

Similarly, molecular mass of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is:

$$= 12(12.011 \text{ u}) + 22(1.008 \text{ u}) + 11(16.00 \text{ u})$$

$$= 144.1324 + 22.176 + 176$$

$$= 342.308 \text{ u}$$

ILLUSTRATION 1.27

Calculate molecular mass of the following molecules:

- Sulphuric acid (H_2SO_4)
- Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)
- Methane (CH_4)

Sol.

- a. Molecular mass of H_2SO_4
 $= 2(1.008 \text{ u}) + 32.0 \text{ u} + 4(16.0 \text{ u})$
 $= 2.016 \text{ u} + 32.0 \text{ u} + 64.0 \text{ u} = 98.016 \text{ u}$
- b. Molecular mass of $\text{C}_6\text{H}_{12}\text{O}_6$
 $= 6(12.011 \text{ u}) + 12(1.008 \text{ u}) + 6(16.00 \text{ u})$
 $= 72.066 \text{ u} + 12.096 \text{ u} + 96.00 \text{ u} = 180.162 \text{ u}$
- c. Molecular mass of CH_4
 $= (12.011 \text{ u}) + 4(1.008 \text{ u}) = 16.043 \text{ u}$

1.8.4 GRAM MOLECULAR MASS

The molecular mass of a compound expressed in grams is called gram molecular mass. The amount of the compound is also called *one gram molecule*, e.g., gram molecular mass of $\text{C}_6\text{H}_{12}\text{O}_6$ or one gram molecule of $\text{C}_6\text{H}_{12}\text{O}_6 = 180.162 \text{ g}$.

1.8.5 FORMULA MASS AND GRAM FORMULA MASS

Ionic compounds, e.g., NaCl , KCl , KNO_3 , ZnS , CaF_2 , etc., do not contain discrete molecules as their constituent particles but exist as ions. Each ion is surrounded by a number of oppositely charged ions. In NaCl , each Na^+ ion is surrounded by 6Cl^- ions and vice versa. Similarly, in ZnS , each Zn^{2+} ion is surrounded by 4S^{2-} ions and vice versa. Hence, in such cases, the formula is used to calculate the formula mass instead of molecular mass. Like the molecular mass, formula mass is calculated by adding the atomic masses of the atoms present in one formula unit, e.g.,

Formula mass of NaCl

$$= \text{Atomic mass of Na} + \text{Atomic mass of Cl}$$

$$= 23.0 \text{ u} + 35.5 \text{ u} = 58.5 \text{ u}$$

Formula mass of a substance expressed in grams is called gram formula mass.

1.9 MOLE CONCEPT

In SI system, mole (symbol, mol) was introduced as the seventh base quantity for the amount of a substance.

One gram atom of any element contains the same number of atoms and one gram molecule of any substance contains the same number of molecules. This number has been experimentally determined and found to be equal to 6.022137×10^{23} correct up to 7 significant figures. However, the value generally used is 6.022×10^{23} and is called *Avogadro number* or constant, denoted by (N_A or N) in honour of Amedeo Avogadro.

Thus, amount of substance containing Avogadro's number of atoms or molecules is called a mole. Hence, a mole is a chemist's unit for counting entities at the microscopic level, such as atoms, molecules, ions, electrons, protons, neutrons, etc., just as one dozen for 12 items, score for 20 items, gross for 144 items.

Thus, one mole is the amount of a substance that contains as many entities or particles as there are atoms in exactly 12 g (or 0.012 kg) of the ^{12}C isotope.

To determine the number precisely, the mass of a C-12 was determined by a mass spectrometer and found to be equal to $1.992648 \times 10^{-23} \text{ g}$.

Number of atoms in one mole of carbon

$$= \frac{12 \text{ g mol}^{-1} \text{ of } ^{12}\text{C}}{1.992648 \times 10^{-23} \text{ g } (^{12}\text{C atom})^{-1}}$$

$$= 6.0221367 \times 10^{23} \text{ atoms mol}^{-1}$$

$$\approx 6.022 \times 10^{23} \text{ atoms mol}^{-1}$$

(rounding off to 4 significant figures)

Thus, 1 mol (or 1 g atom) of C atoms = 6.022×10^{23} C atoms

1 mol (or 1 g atom) of Na atoms = 6.022×10^{23} Na atoms

1 mol (or 1 g molecule) of H_2O molecules

$$= 6.022 \times 10^{23} \text{ water molecules}$$

1 mol (or 1 g molecule) of NaCl molecules

$$= 6.022 \times 10^{23} \text{ formula units of NaCl}$$

1.9.1 MOLAR MASS

The mass of one mole of a substance in grams is called its molar mass.

The molar mass in grams is numerically equal to atomic or molecular formula mass in u. Units of molar mass are g mol^{-1} or kg mol^{-1} .

$$\therefore \text{Molar mass of } \text{CO}_2 = 12.011 + 2(16.0) = 44.011 \text{ g mol}^{-1}$$

$$\text{Molar mass of NaCl} = 23.0 + 35.5 = 58.5 \text{ g mol}^{-1}$$

ILLUSTRATION 1.28

Calculate molecular mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) molecule.

Sol.

Molecular mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)

$$= 6(12.011 \text{ u}) + 12(1.008 \text{ u}) + 6(16.00 \text{ u})$$

$$= (72.066 \text{ u}) + (12.096 \text{ u}) + (96.00 \text{ u})$$

$$= 180.162 \text{ u}$$

1.9.2 MOLAR VOLUME

According to Avogadro's hypothesis, equal volumes of different gases under similar conditions of temperature and pressure contain equal number of molecules. Thus, 1 mol of any gas at STP (standard temperature and pressure), viz., 1 atm and 273 K (0°C) contains N_A molecules (6.022×10^{23}).

Alternatively N_A molecules of any gas at STP have the same volume. This volume has been experimentally found to be 22.4 L at STP (1 atm, 273 K or 1.01 bar, 273 K) and is called *molar volume*. In general, molar volume of any gas is the volume of one mole of a gas at STP.

For example,

$$1 \text{ mol of } \text{O}_2 \text{ gas} = 32 \text{ g} = N_A \text{ molecules} = 22.4 \text{ L of volume at STP}$$

$$1 \text{ mol of } \text{CO}_2 \text{ gas} = 44 \text{ g} = N_A \text{ molecules} = 22.4 \text{ L of volume at STP}$$

Note: Loschmidt Number: The number of molecules present in 1 cm^3 of an ideal gas at STP is called Loschmidt number

$$= \frac{6.022 \times 10^{23}}{22400 \text{ mL}} = 2.69 \times 10^{19}$$

Thus, mole concept can be summarised as:

1 mol (or 1 g atom) of any element

$$= N_A \text{ atoms } (6.022 \times 10^{23})$$

= Gram atomic mass of the element

1 mol (or 1 g molecule) of any compound

$$= N_A \text{ molecules } (6.022 \times 10^{23})$$

= Gram molar mass of the compound

1 mol of any gas

$$= N_A \text{ molecules} = \text{Gram molar mass of the gas}$$

$$= 22.4 \text{ L volume of gas at STP}$$

ILLUSTRATION 1.29

In 4 g atoms of Ag, calculate

- Amount of Ag.
- Weight of one atom of Ag (atomic weight of Ag = 108).

Sol.

$$\text{a. } 4 \text{ g atom} = 4 \text{ mol of Ag}$$

$$1 \text{ mol of Ag} = 108 \text{ g}$$

$$4 \text{ mol of Ag} = 108 \times 4 = 432 \text{ g}$$

$$\text{b. } 1 \text{ mol of Ag} = 6.022 \times 10^{23} \text{ atoms}$$

$$\therefore 6.023 \times 10^{23} \text{ atoms} \Rightarrow 108 \text{ g}$$

$$1 \text{ atom} \Rightarrow \frac{108}{6.022 \times 10^{23}} \text{ g} \Rightarrow 17.93 \times 10^{-23} \text{ g}$$

ILLUSTRATION 1.30

How many g atoms are there in one atom?

$$\text{Sol. } 6.023 \times 10^{23} \text{ atoms} = 1 \text{ g atom} = 1 \text{ mole}$$

$$1 \text{ atom} = \frac{1}{6.023 \times 10^{23}}$$

$$= 1.66 \times 10^{-24} \text{ g atom or mol}$$

ILLUSTRATION 1.31

How many years it would take to spend Avogadro's number of rupees at the rate of 10 lakh rupees per second?

$$\text{Sol. } 10 \text{ lakh} = 10 \times 100000 = 10^6$$

$$1 \text{ Avogadro's number of rupees} = 6.023 \times 10^{23}$$

$$10^6 \text{ rupees} \Rightarrow 1 \text{ s}$$

$$6.023 \times 10^{23} \text{ rupees} = \frac{1 \times 6.023 \times 10^{23}}{10^6} \text{ s}$$

$$= \frac{6.023 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365} \text{ years}$$

$$= 1.9099 \times 10^{10} \text{ years}$$

ILLUSTRATION 1.32

From 200 mg of CO_2 , 10^{21} molecules are removed. How many grams and moles of CO_2 are left.

$$\text{Sol. } 44 \text{ g of } \text{CO}_2 = 1 \text{ mol} = 6.023 \times 10^{23} \text{ molecules}$$

$$\therefore 6.023 \times 10^{23} \text{ molecules} = 44 \text{ g of } \text{CO}_2$$

$$10^{21} \text{ molecules} = \frac{40 \times 10^{21} \times 10^3}{6.023 \times 10^{23}} \text{ mg}$$

$$\text{Weight of } \text{CO}_2 \text{ left} = 200 - 73.05 = 126.9 \text{ mg}$$

$$= \frac{126.9}{10^3} = 0.1269 \text{ g}$$

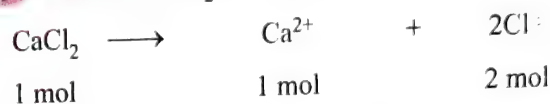
$$44 \text{ g of } \text{CO}_2 = 1 \text{ mol}$$

$$0.1269 \text{ g of } \text{CO}_2 = \frac{1}{44} \times 0.1269 = 0.0028 \text{ mol}$$

ILLUSTRATION 1.33

Calculate the number of Cl^- and Ca^{2+} ions in 222 g anhydrous CaCl_2 .

$$\text{Sol. } 1 \text{ mole of } \text{CaCl}_2 = 40 + 35.5 \times 2 = 111 \text{ g}$$



$$\text{a. } 111 \text{ g of } \text{CaCl}_2 \Rightarrow 1 \text{ mol of } \text{Ca}^{2+}$$

$$222 \text{ g of } \text{CaCl}_2 \Rightarrow 2 \text{ mol of } \text{Ca}^{2+}$$

$$\text{b. } 111 \text{ g of } \text{CaCl}_2 \Rightarrow 2 \text{ mol of } \text{Cl}^-$$

$$222 \text{ g of } \text{CaCl}_2 = \frac{2}{111} \times 222 = 4 \text{ mol of } \text{Cl}^-$$

$$\text{Therefore, number of } \text{Ca}^{2+} \text{ ions} = 2 \times N$$

$$= 2N \text{ or } 2 \times 6 \times 6.023 \times 10^{23}$$

$$\text{Number of } \text{Cl}^- \text{ ions} = 4 \times N$$

$$= 4N \text{ or } 4 \times 6.023 \times 10^{23}$$

ILLUSTRATION 1.34

The dot at the end of this sentence has a mass of about one microgram. Assuming that black stuff is carbon, calculate approximate atoms of carbon needed to make such a dot.

$$\text{Sol. } 1 \text{ micro gram} = 1 \mu\text{g} = 10^{-6} \text{ g}$$

$$1 \text{ mole of C} = 12 \text{ g} = 6.023 \times 10^{23} \text{ atoms}$$

$$12 \text{ g of C} = 6.023 \times 10^{23} \text{ atoms}$$

$$10^{-6} \text{ g of C} = \frac{6.023 \times 10^{23} \times 10^{-6}}{12} = 5 \times 10^{16} \text{ atoms of C}$$

ILLUSTRATION 1.35

Calculate mass of sodium which contains same number of atoms as are present in 4 g of calcium (Atomic weight Na = 23, atomic weight Ca = 40)

Sol.

$$\text{a. } 40 \text{ g of Ca} = 6.023 \times 10^{23} \text{ atoms}$$

$$4 \text{ g of Ca} = 6.023 \times 10^{22} \text{ atoms}$$

$$\text{b. } 23 \text{ g of Na} = 6.023 \times 10^{23} \text{ atoms}$$

$$\therefore 6.023 \times 10^{23} \text{ atoms of Na}$$

$$= 23 \text{ g}$$

$$= 6.023 \times 10^{22} \text{ atoms of Na}$$

$$= 2.3 \text{ g}$$

ILLUSTRATION 1.36

Calculate the number of moles in each of the following:

- 11 g of CO_2
- 3.01×10^{22} molecules of CO_2
- 1.12 L of CO_2 at STP

Sol.

- 44 g of $\text{CO}_2 = 1 \text{ mol}$
 $11 \text{ g of CO}_2 = \frac{1}{44} \times 11 = \frac{1}{4} = 0.25 \text{ mol}$
- 6.023×10^{23} molecules = 1 mol
 $3.01 \times 10^{22} \text{ molecules} = \frac{1 \times 3.01 \times 10^{22}}{6.023 \times 10^{23}} = 0.05 \text{ mol}$
- 22.4 L of $\text{CO}_2 = 1 \text{ mol}$
 $1.12 \text{ L of CO}_2 = \frac{1 \times 1.12}{22.4} = 0.05 \text{ mol}$

ILLUSTRATION 1.37

Calculate the mass of the following:

- One atom of calcium
- One molecule of SO_2

Sol.

- 6.023×10^{23} atoms of Ca $\Rightarrow 40 \text{ g}$
 $1 \text{ atom of Ca} \Rightarrow \frac{40}{6.023 \times 10^{23}} \Rightarrow 6.6 \times 10^{-23} \text{ g}$
- 6.023×10^{23} molecules of $\text{SO}_2 \Rightarrow 64 \text{ g}$
 $1 \text{ molecule} \Rightarrow \frac{64}{6.023 \times 10^{23}}$
 $\Rightarrow 1.06 \times 10^{-23} \text{ g}$

ILLUSTRATION 1.38

- Calculate number of atoms in each of the following:
 - 0.5 mol atom of nitrogen
 - 0.2 mol molecules of hydrogen
 - 3.2 g of sulphur
- Calculate number of molecules in each of the following:
 - 14 g of nitrogen
 - 3.4 g of H_2S

Sol.

- 1 mol of $\text{N}_2 = 6.023 \times 10^{23}$ molecules or mole atom
 $0.5 \text{ mol atom of N}_2 = 6.023 \times 10^{23} \times 0.5$
 $= 3.01 \times 10^{23} \text{ atoms}$
 - 1 mol of $\text{H}_2 = 6.023 \times 10^{23}$ molecules
 $= 2 \times 6.023 \times 10^{23} \text{ atoms}$
 $0.2 \text{ mol of H}_2 = 2 \times 6.023 \times 10^{23} \times 0.2$
 $= 2.409 \times 10^{23} \text{ atoms}$

$$\text{iii. } 32 \text{ g of S} = 6.023 \times 10^{23} \text{ atoms}$$

$$3.2 \text{ g of S} = 6.023 \times 10^{22} \text{ atoms}$$

- 1 mol of $\text{N}_2 = 28 \text{ g}$
 - 28 g of $\text{N}_2 = 6.023 \times 10^{23}$ molecules
 $14 \text{ g of N}_2 = \frac{6.023 \times 10^{23}}{28} \times 14$
 $= 3.01 \times 10^{23} \text{ molecules}$
 - 34 g of $\text{H}_2\text{S} \Rightarrow 6.023 \times 10^{23}$ molecules
 $3.4 \text{ g of H}_2\text{S} \Rightarrow 6.023 \times 10^{22}$ molecules

ILLUSTRATION 1.39

How many moles of O are present in 4.9 g of H_3PO_4 ? (At. weight of P, O, and H = 31, 16, 1)

Sol. Molecular weight of $\text{H}_3\text{PO}_4 = 1 \times 3 + 31 + 16 \times 4 = 98$
 $98 \text{ g} = 1 \text{ mole of H}_3\text{PO}_4 = 4 \text{ mole of O}$

$$4.9 \text{ g of H}_3\text{PO}_4 = \frac{4}{98} \times 4.9 = 0.2 \text{ mole of O}$$

ILLUSTRATION 1.40

What is the molecular mass of a compound X, if 3.0115×10^9 molecules weigh $1.0 \times 10^{-12} \text{ g}$?

Sol. 3.0115×10^9 molecules of $X = 10^{-12} \text{ g}$
 6.023×10^{23} molecules of $X = \frac{10^{-12} \times 6.023 \times 10^{23}}{3.0115 \times 10^9}$
 $= 200 \text{ g} = 200 \text{ amu}$

ILLUSTRATION 1.41

What is the volume occupied by one CCl_4 molecule at 20°C ? Density of CCl_4 is 1.6 g mL^{-1} at 20°C .

Sol. CCl_4 molecule is liquid.

$$M_w \text{ of CCl}_4 = 12 + 4 \times 35.5 = 154 \text{ g}$$

$$6.023 \times 10^{23} \text{ molecules of CCl}_4 = 154 \text{ g}$$

$$1 \text{ molecule of CCl}_4 = \frac{154}{6.023 \times 10^{23}} = 25.56 \times 10^{-23} \text{ g}$$

$$\text{Volume of one molecule} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{25.56 \times 10^{-23}}{1.6}$$

$$= 1.598 \times 10^{-22} \text{ mL or cm}^3$$

ILLUSTRATION 1.42

How many grams of $\text{Cu}(\text{NO}_3)_2$ would you need to take to get 1.00 g of copper? Cu = 63.5, N = 14, O = 16.

Sol. $M_w \text{ of Cu}(\text{NO}_3)_2 = 63.5 + 2(14 + 16 \times 3) = 187.5 \text{ g}$

$$\begin{array}{ccc} \text{Cu}(\text{NO}_3)_2 & \longrightarrow & \text{Cu} \\ 1 \text{ mol} & & 1 \text{ mol} \\ = 187.5 \text{ g} & & = 63.5 \text{ g} \end{array}$$

$$63.5 \text{ g of Cu is obtained from } 187.5 \text{ g of Cu}(\text{NO}_3)_2$$

$$1 \text{ g of Cu is obtained from} = \frac{187.5}{63.5} = 2.9528 \text{ g}$$

ILLUSTRATION 1.43

✓ Calculate the number of atoms of each type that are present in 3.42 g of sucrose ($C_{12}H_{22}O_{11}$).

Sol. M_w of sucrose = $C_{12}H_{22}O_{11}$
 $= 12 \times 12 + 1 \times 22 + 16 \times 11$
 $= 342 \text{ g}$

a. 1 mol of sucrose = 342 g = 12 mol of C

$$\therefore 3.42 \text{ g} = \frac{12}{342} \times 3.42$$

$$= 0.12 \text{ mol of C} = 0.12 \times 6.023 \times 10^{23} \text{ atoms}$$

$$= 7.228 \times 10^{22} \text{ atoms of C}$$

b. 342 g of sucrose = 22 mol of H

$$3.42 \text{ g of sucrose} = \frac{22}{342} \times 3.42$$

$$= 0.22 \text{ mol of H}$$

$$= 0.22 \times 6.023 \times 10^{23} \text{ atoms}$$

$$= 132.5 \times 10^{21} \text{ atoms of H}$$

c. 342 g of sucrose = 11 mol of O

$$= 11 \times 6.023 \times 10^{23} \text{ atoms of O}$$

$$3.42 \text{ g of sucrose} = \frac{11 \times 6.023 \times 10^{23}}{342} \times 3.42$$

$$= 66.25 \times 10^{21} \text{ atoms of O}$$

ILLUSTRATION 1.44

How many molecules of benzene (C_6H_6) are there in 1 L of benzene? Specific gravity of benzene is 0.88.

Sol. M_w of benzene (C_6H_6) = $12 \times 6 + 1 \times 6 = 78 \text{ g}$

1 litre of benzene = 1000 mL

Mass of 1000 mL of benzene = volume \times density
 $= 1000 \times 0.88 = 880 \text{ g}$

$\therefore 78 \text{ g of benzene} = 6.023 \times 10^{23} \text{ molecules}$

$$880 \text{ g of benzene} = \frac{6.023 \times 10^{23} \times 880}{78}$$

$$= 6.795 \times 10^{24} \text{ molecules}$$

ILLUSTRATION 1.45

The volume of a drop of water is 0.04 mL. How many H_2O molecules are there in a drop of water? $d = 1.0 \text{ g mL}^{-1}$.

Sol. Volume of 1 drop of $H_2O = 0.04 \text{ mL}$

Weight of 1 drop of $H_2O = \text{Volume} \times \text{Density}$
 $= 0.04 \times 1 = 0.04 \text{ g}$

1 mole of $H_2O = 18 \text{ g} = 6.023 \times 10^{23} \text{ molecules}$

$$\therefore 0.04 \text{ g} = \frac{6.023 \times 10^{23} \times 0.04}{18} = 1.3384 \times 10^{21} \text{ molecules}$$

ILLUSTRATION 1.46

Find the volume of the following at STP.

a. 14 g of nitrogen

b. 6.023×10^{22} molecules of NH_3

c. 0.1 mole of SO_2 .

Sol.

a. 1 mole of $N_2 \Rightarrow 28 \text{ g} = 22.4 \text{ L at STP}$

14 g = 11.2 L

b. 1 mole of $NH_3 = 17 \text{ g}$

$= 6.023 \times 10^{23} \text{ molecules} = 22.4 \text{ L}$

$\therefore 6.023 \times 10^{22} \text{ molecules} = 2.24 \text{ L}$

c. 1 mole of $SO_2 = 32 + 16 \times 2 = 64 \text{ g} = 22.4 \text{ L}$

0.1 mole of $SO_2 = 2.24 \text{ L}$

ILLUSTRATION 1.47

a. What is the volume of one molecule of water.

(density of $H_2O = 1 \text{ g cm}^{-3}$)

b. What is the radius of the water molecule assuming it be spherical.

c. Calculate the radius of the oxygen atom, assuming that oxygen atom occupies half of the volume occupied by the water molecule.

Sol.

a. 1 mole of $H_2O = 18 \text{ g} = 18 \text{ cm}^3$

($\because d_{H_2O} = 1 \text{ g cm}^{-3}$)

$= 6.022 \times 10^{23} \text{ molecules of } H_2O$

Therefore, volume of 1 molecule of H_2O

$$= \frac{18}{6.022 \times 10^{23}} \text{ cm}^3$$

$$= 2.989 \times 10^{-23} \text{ cm}^3$$

b. Since H_2O molecule is spherical, if its radius is r , then volume will be

$$\frac{4}{3} \pi r^3 = 2.989 \times 10^{-23} \text{ cm}^3$$

or $r^3 = 7.133 \times 10^{-24}$

or $r = (7.133 \times 10^{-24})^{\frac{1}{3}} = (7.133)^{\frac{1}{3}} \times 10^{-8} \text{ cm}$

Put $x = (7.133)^{\frac{1}{3}}$

$$\log x = \frac{1}{3} \log 7.133 = \frac{1}{3} \times 0.8533 = 0.2844$$

$x = \text{Antilog } 0.2844 = 1.925$

$\therefore r = 1.925 \times 10^{-8} \text{ cm}$

c. Let R is the radius of the oxygen atom, and the oxygen atom occupies half the volume of H_2O molecule, then

$$\frac{4}{3} \pi R^3 = \frac{1}{2} \times 2.989 \times 10^{-23} \text{ cm}^3$$

$R^3 = 3.566 \times 10^{-24} \text{ cm}^3$

$R = 1.528 \times 10^{-8} \text{ cm}$

ILLUSTRATION 1.48

Calculate the mass of carbon present in 0.1 mole of sodium ferricyanide $Na_3[Fe(CN)_6]$.

Sol. 1 mole of $Na_3[Fe(CN)_6]$ contains = 6 mol of C

0.1 mole of $Na_3[Fe(CN)_6]$ contains = 0.6 mol of C

$$= 0.6 \times 12 = 7.2 \text{ g}$$

ILLUSTRATION 1.49

Calculate the total number of electrons present in 3.2 g of oxygen gas.

Sol. (Atomic number of O = 8, Number of electrons in $\text{O}_2 = 16$)

$$\begin{aligned} 3.2 \text{ g of } \text{O}_2 &= \frac{3.2}{32} = 0.1 \text{ mol} \\ &= 0.1 \times 6.022 \times 10^{23} \text{ molecules} \\ &= 6.022 \times 10^{22} \text{ molecules} \\ &= 6.022 \times 10^{22} \times 16 \text{ electrons} \\ &= 9.635 \times 10^{23} \text{ electrons} \end{aligned}$$

ILLUSTRATION 1.50

- Calculate the number of molecules present in one drop of H_2O whose mass is 0.01 g.
- Calculate the number of molecules leaving the liquid surface per second, if the same drop of water evaporates in one hour.

Sol.

- $$0.01 \text{ g of } \text{H}_2\text{O} = \frac{0.01}{18} \text{ mol}$$

$$= \frac{0.01}{18} \times 6.022 \times 10^{23} \text{ molecules}$$

$$= 3.345 \times 10^{20} \text{ molecules}$$
- $$\text{Number of molecules leaving per second} = \frac{3.345 \times 10^{20}}{60 \times 60} = 9.293 \times 10^{16} \text{ molecules}$$

CONCEPT APPLICATION EXERCISE 1.1**Subjective Type**

- A metal M of atomic weight 54.9 has a density of 7.42 g cm^{-3} . Calculate the volume occupied and the radius of the atom of this metal assuming it to be sphere.

Objective Type

- Which of the following has least mass?
 - 1 mol of S
 - 3×10^{23} atoms of C
 - 2 g atom of nitrogen
 - 7.0 g of Ag
- The simplest formula of a compound containing 50% of element A (atomic mass 10) and 50% of element B (atomic mass 20) is:
 - AB
 - A_2B
 - A_2B_3
 - AB_3
- The number of water molecules present in a drop of water (volume 0.0018 mL) at room temperature is:
 - 6.023×10^{19}
 - 5.023×10^{23}
 - 1.084×10^{18}
 - 4.84×10^{17}

Fill in the Blanks Type

- The mass of 1 molecule of water (H_2O) is
- The number of molecules in 16 g of sulphur dioxide (SO_2) are
- The weight of one mole of sodium carbonate (Na_2CO_3) is

- Moles and g equivalents in 196 g of $\text{Ca}(\text{OH})_2$ are and
- Moles and g equivalents in 196 g of H_3PO_4 are and
- g atoms in 62 g of P₄ are
- g atoms in 24 g of magnesium are

ANSWERS**Subjective Type**

- $1.23 \times 10^{-23} \text{ cm}^3$, $1.42 \times 10^{-8} \text{ cm}$

Objective Type

- i. (2), ii. (2), iii. (1)

Fill in the Blanks Type

- a. 3×10^{-23} , b. 1.5×10^{23} , c. 106 g
d. 2.65, 5.3, e. 2, 6, f. 0.5, g. 1

1.10 PERCENTAGE COMPOSITION

For an unknown or new compound, it is necessary to know its formula or to know the ratios of their constituents in the given compound. Such information provides a check whether the given sample contains the same percentage of elements as is present in a pure sample. Therefore, it helps in checking the purity of a sample by analysing this data.

The percentage of any element or constituent in a compound is the number of parts by mass of that element or constituent present in 100 parts by mass of the compound.

It is calculated as follows:

- First calculate the molecular mass of the compound from its formula by adding the atomic masses of the elements present in it, multiplied by their respective number.
- Then calculate the percentage of the element or constituents by using the relation:

$$\text{Mass\% of an element} = \frac{\text{Mass of that element} \times 100 \text{ in the compound}}{\text{Molar mass of the compound}}$$

For example, the percentage composition of the various elements in H_2O .

$$\text{Molar mass of } \text{H}_2\text{O} = 18.02 \text{ g}$$

$$\text{Mass\% of H} = \frac{2 \times 1.008}{18.02} \times 100 = 11.18\%$$

$$\text{Mass\% of O} = \frac{16.00 \times 100}{18.02} \times 88.79\%$$

ILLUSTRATION 1.51

Calculate the percentage composition of various elements in the following compounds:

- Blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
- Green vitriol ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
- White vitriol ($\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$)
- Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
- Mohr's salt

Sol. a. Molar mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 63.5 + 32 + 4 \times 16 + 5 \times 18$

$$249.5 \text{ g}$$

$$\text{Mass\% of Cu} = \frac{63.5 \times 100}{249.5} = 25.45\%$$

$$\text{Mass\% of S} = \frac{32 \times 100}{249.5} = 12.82\%$$

$$\text{Mass\% of O} = \frac{16 \times 9 \times 100}{249.5} = 57.71\%$$

$$\text{Mass\% of H} = \frac{10 \times 1.008 \times 100}{249.5} = 4.040\%$$

b. Molar mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 56 + 32 + 64 + 7 \times 18$

$$278 \text{ g}$$

$$\text{Mass\% of Fe} = \frac{56 \times 100}{278} = 20.1\%$$

$$\text{Mass\% of S} = \frac{32 \times 100}{278} = 11.5\%$$

$$\text{Mass\% of O} = \frac{11 \times 16 \times 100}{278} = 63.3\%$$

$$\text{Mass\% of H} = \frac{14 \times 1.008 \times 100}{278} = 5.0\%$$

c. Molar mass of $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O} = 65.37 + 32 + 64 + 5 \times 18$

$$= 251.37 \text{ g}$$

$$\text{Mass\% of Zn} = \frac{65 \times 37 \times 100}{251.37} = 26.0\%$$

$$\text{Mass\% of S} = \frac{32 \times 100}{251.37} = 12.7\%$$

$$\text{Mass\% of O} = \frac{16 \times 9 \times 100}{251.37} = 57.2\%$$

$$\text{Mass\% of H} = \frac{10 \times 1.008 \times 100}{251.37} = 4.01\%$$

d. Molar mass of $\text{C}_2\text{H}_5\text{OH} = 2 \times 12.01 + 6 \times 1.008 + 16.00 \text{ g}$

$$= 46.068 \text{ g}$$

$$\text{Mass\% of C} = \frac{24.02 \text{ g}}{46.068 \text{ g}} \times 100 = 52.14\%$$

$$\text{Mass\% of H} = \frac{6.048 \text{ g}}{46.068 \text{ g}} \times 100 = 13.13\%$$

$$\text{Mass\% of O} = \frac{16.00 \text{ g}}{46.068 \text{ g}} \times 100 = 34.73\%$$

e. Molar mass of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

$$= 2(14 + 4) + 32 + 16 \times 4 + 56 + 32 + 64 + 108 = 392 \text{ g}$$

$$\text{Mass\% of N} = \frac{28 \text{ g}}{392 \text{ g}} \times 100 = 7.14\%$$

$$\text{Mass\% of H} = \frac{20 \times 1.0 \text{ g}}{392 \text{ g}} \times 100 = 5.10\%$$

$$\text{Mass\% of S} = \frac{2 \times 32 \text{ g}}{392 \text{ g}} \times 100 = 16.32\%$$

$$\text{Mass\% of O} = \frac{14 \times 16.00 \text{ g}}{392 \text{ g}} \times 100 = 57.14\%$$

$$\text{Mass\% of Fe} = \frac{56 \text{ g}}{382 \text{ g}} \times 100 = 14.28\%$$

ILLUSTRATION 1.52

Calculate the percentage composition of:

- Alumina (Al_2O_3), potassium oxide (K_2O), and silica (SiO_2) in the sample of clay ($\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2$).
- Potassium sulphate (K_2SO_4), aluminium sulphate, and water of crystallisation in the sample of potash alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$).
- SO_4^{2-} ion in potash alum.

Sol.

a. Molar mass of $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2$

$$= (2 \times 27 + 3 \times 16) + (2 \times 39 + 16) + 6(28 + 2 \times 16)$$

$$= 102 + 94 + 360 = 556 \text{ g}$$

$$\text{Mass\% of Al}_2\text{O}_3 = \frac{102}{556} \times 100 = 18.35\%$$

$$\text{Mass\% of K}_2\text{O} = \frac{94}{556} \times 100 = 16.90\%$$

$$\text{Mass\% of SiO}_2 = \frac{360}{556} \times 100 = 64.75\%$$

b. Molar mass of $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

$$= (2 \times 39 + 32 + 64) + [2 \times 27 + 3(32 + 64) + 24 \times 18]$$

$$= 174 + 342 + 432 = 948 \text{ g}$$

$$\text{Mass\% of K}_2\text{SO}_4 = \frac{174}{948} \times 100 = 18.35\%$$

$$\text{Mass\% of Al}_2(\text{SO}_4)_3 = \frac{342}{948} \times 100 = 36.07\%$$

$$\text{Mass\% of H}_2\text{O} = \frac{432}{948} \times 100 = 45.56\%$$

c. Molar mass of $4(\text{SO}_4^{2-}) = 4(32 + 64) = 384 \text{ g}$

$$\text{Mass\% of SO}_4^{2-} = \frac{384}{948} \times 100 = 40.50\%$$

1.11 EMPIRICAL AND MOLECULAR FORMULAE

Empirical formula: It represents the simplest whole number ratio of the various atoms present in a compound.

For example, the empirical formula of glucose is CH_2O , that of benzene is CH , and that of hydrogen peroxide is OH .

It is clear that in the molecule of glucose, one atom of carbon is present for every two atoms of hydrogen and one atom of oxygen. Similarly, in the molecule of benzene, one carbon atom is present for every one atom of hydrogen, and in the molecule of hydrogen peroxide, one atom of hydrogen is present for one atom of oxygen.

Thus, the empirical formula of a compound represents only the atomic ratio of the various elements present in its molecule.

Molecular formula: It represents the exact number of different types of atoms present in a molecule of a compound. For example, molecular formula of glucose is $C_6H_{12}O_6$, that of benzene is C_6H_6 , and that of hydrogen peroxide is H_2O_2 .

It is clear that one molecule of glucose contains six atoms of C, 12 atoms of H and 6 atoms of O. Similarly one molecule of benzene contains 6 atoms of C and 6 atoms of H, and one molecule of H_2O_2 contains 2 atoms of H and 2 atoms of O.

1.11.1 RELATION BETWEEN EMPIRICAL AND MOLECULAR FORMULAE

The molecular formula of a compound is a simple whole number multiple of its empirical formula,

$$\text{Molecular formula} = n \times \text{Empirical formula}$$

where n is any integer, e.g., 1, 2, 3, ..., etc.

The value of n is obtained as

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

1.11.2 MOLAR MASS OF A VOLATILE COMPOUND

It is determined by Victor Meyer's method. It is based on the principle that 22.4 L of vapours of a volatile compound at STP have mass equal to the gram molecular mass or by the relation given below.

$$\text{Molar mass} = 2 \times \text{Vapour density}$$

1.11.3 CALCULATION OF THE EMPIRICAL AND MOLECULAR FORMULAE

If the mass percentage of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following sequence of steps are involved in the calculation of empirical and molecular formula.

ILLUSTRATION 1.53

A compound contains 4.07% H, 24.27% C and 71.65% Cl. Its molar mass is 98.96 g. What are the empirical and molecular formulas?

Sol.

a. Conversion of mass percent to grams:

Take 100 g of the starting material. The given mass percentage represents the masses of the elements in grams. For example, a compound contains 4.07% H, 24.27% C, and 71.65% Cl.

So, 100 g of the above compound, 4.07 g of H, 24.27 g of C and 71.65 g of Cl is present.

b. Convert into number of moles of each element:

Divide the masses obtained by respective atomic masses of various elements.

$$\text{Moles of H} = \frac{4.07 \text{ g}}{1.008 \text{ g}} = 4.04$$

$$\text{Moles of C} = \frac{24.27 \text{ g}}{12.01 \text{ g}} = 2.021$$

$$\text{Moles of Cl} = \frac{71.65 \text{ g}}{35.453 \text{ g}} = 2.021$$

c. To calculate the simplest whole number:

Divide the moles obtained in step (b) by the smallest quotient or least value from amongst the values obtained for each element. This gives the simplest molar ratio. For example, since 2.021 is smallest value, division by it gives a ratio of 2 : 1 : 1 for H : C : Cl.

If the ratios are not whole numbers, then they are converted into whole number by multiplying by a suitable coefficient.

d. Writing empirical formula:

It is written by mentioning the numbers after writing the symbols of respective elements.

Thus, CH_2Cl is the empirical formula of the above compound.

e. Writing molecular formula:

i. Determine the empirical formula mass (EFM).

Add the atomic masses multiplied by their respective numbers of various atoms present in the empirical formula.

$$\begin{aligned} \text{For } CH_2Cl, \text{ EFM} &= 12.01 + 2 \times 1.008 + 35.453 \\ &= 49.48 \text{ g} \end{aligned}$$

ii. Divide the molar mass by EFM.

$$\frac{\text{Molar mass}}{\text{EFM}} = \frac{98.86}{49.48} = 2 = (n)$$

iii. Multiply EF by n to get molecular formula (MF).

$$\text{Hence, MF} = 2 \times (CH_2Cl) = C_2H_4Cl_2$$

ILLUSTRATION 1.54

A substance, on analysis, gave the following percentage composition: Na = 43.4%, C = 11.3%, and O = 45.3%. Calculate the empirical formula (atomic weight Na = 23, C = 12, O = 16).

Sol.

Element	Percentage composition	Atomic ratio	Least ratio
Sodium	43.4	$\frac{43.4}{23} = 1.89$	$\frac{1.89}{0.94} = 2$
Carbon	11.3	$\frac{11.3}{12} = 0.94$	$\frac{0.94}{0.94} = 1$
Oxygen	45.3	$\frac{45.3}{16} = 2.83$	$\frac{2.83}{0.94} = 3$

Hence, the empirical formula is Na_2CO_3 .

ILLUSTRATION 1.55

Assuming the atomic weight of a metal M to be 56, find the empirical formula of its oxide containing 70.00% of M.

Sol. Percentage of metal M = 70.00 and that of oxygen = 30.00.

Element	%	Atomic ratio	Least ratio	Whole number ratio
Metal	70.00	$\frac{70}{56} = 1.25$	$\frac{1.25}{1.25} = 1$	2
Oxygen	30.00	$\frac{30}{16} = 1.875$	$\frac{1.875}{1.25} = 1.5$	3

Hence, empirical formula = M_2O_3 .

ILLUSTRATION 1.56

An organic compound containing oxygen, carbon, hydrogen, and nitrogen contains 20% carbon, 6.7% hydrogen, and 46.67% nitrogen. Its molecular weight was found to be 60. Find the molecular formula of the compound.

Sol.

Element	% Composition	Atomic ratio	Least ratio	Empirical formula
Carbon	20.00	$\frac{20.00}{12} = 1.66$	$\frac{1.66}{1.66} = 1$	CH_4N_2O
Hydrogen	6.70	$\frac{6.7}{1} = 6.7$	$\frac{6.7}{1.66} = 4$	
Nitrogen	46.67	$\frac{46.67}{14} = 3.33$	$\frac{3.33}{1.66} = 2$	
Oxygen	$100 - (20.0 + 6.7 + 46.7) = 26.63$	$\frac{26.63}{16} = 1.66$	$\frac{1.66}{1.66} = 1$	

Empirical formula weight = $12 + 4 + 28 + 16 = 60$

Molecular mass = 60 (given)

Therefore, empirical formula mass is same as molar mass.

Hence, molecular formula is also CH_4N_2O .

ILLUSTRATION 1.57

A compound, on analysis, gave the following percentage composition:

Na = 14.31%

S = 9.97%

H = 6.22%

O = 69.50%

Calculate the molecular formula of the compound on the assumption that all the hydrogen in the compound is reset in combination with oxygen as water of crystallisation. Molecular weight of the compound is 322.

(Na = 23, S = 32, H = 1, O = 16)

Sol.

Element	%	Atomic ratio	Least ratio	Empirical formula
Na	14.31	$\frac{14.31}{23} = 0.622$	$\frac{0.622}{0.311} = 2$	$Na_2SH_{20}O_{14}$
S	9.97	$\frac{9.97}{32} = 0.311$	$\frac{0.311}{0.311} = 1$	
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.311} = 20$	
O	69.50	$\frac{69.50}{16} = 4.34$	$\frac{4.34}{0.311} = 14$	

Empirical formula mass = $46 + 32 + 20 + 224 = 322$

Also, molar mass = 322 (given)

$$\therefore n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{322}{322} = 1$$

Hence, molecular formula = $Na_2SH_{20}O_{14}$

Since, all the hydrogen is in the form of water, there are thus $10H_2O$ molecules.

Hence, the molecular formula is $Na_2SO_4 \cdot 10H_2O$.

ILLUSTRATION 1.58

What is the formula of Kaolin, the composition of which is as follows: $Al_2O_3 = 39.5\%$, $SiO_2 = 46.6\%$, and $H_2O = 13.9\%$ (Al = 27, Si = 28, O = 16, H = 1).

Sol. Empirical formula: Radical weights.

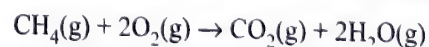
$Al_2O_3 = 54 + 48 = 102$; $SiO_2 = 28 + 32 = 60$; $H_2O = 18$

Element	%	Radical ratio	Least ratio	Empirical or molecular formula
Al_2O_3	39.5	$\frac{39.5}{102} = 0.387$	$\frac{0.387}{0.387} = 1$	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
SiO_2	46.6	$\frac{46.6}{60} = 0.777$	$\frac{0.777}{0.387} = 2$	
H_2O	13.9	$\frac{13.9}{18} = 0.772$	$\frac{0.772}{0.387} = 2$	

ILLUSTRATION 1.59

Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Sol. The balanced equation for combustion of methane is:



(i) 16 g of CH_4 corresponds to 1 mole.

(ii) From the above equation, 1 mol of $CH_4(g)$ gives 2 mol g $H_2O(g)$.

$$2 \text{ mol of H}_2\text{O} = 2 \times (2 + 16) = 36 \text{ g}$$

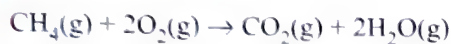
$$1 \text{ mol of CH}_4 = 12 + 4 = 16 \text{ g}$$

Therefore 16 g of CH₄ gives 36 g of H₂O on combustion.

ILLUSTRATION 1.60

How many moles of methane are required to produce 22 g of CO₂ after combustion?

Sol. According to equation:



16 g

44 g

44 g of CO₂ is obtained from 16 g of CH₄(g)

∴ 22 g of CO₂ is obtained from ⇒ 8 g of CH₄(g)

$$\text{Moles of CH}_4(\text{g}) = \frac{8 \text{ g}}{16 \text{ g}} = 0.5 \text{ mol of CO}_2(\text{g})$$

1.12 STOICHIOMETRY AND STOICHIOMETRIC CALCULATIONS

The word 'stoichiometry' is derived from two Greek words—stoicheion (meaning element) and metron (meaning measure). Thus, it deals with the calculation of moles, molecules masses, and sometimes volumes of the reactants and products involved in a balanced chemical equation. The coefficients of the balanced chemical equations are called 'stoichiometric coefficients.' They represent the number of moles and molecules of reactants and products in a balanced chemical equations.

1.12.1 BALANCING OF A CHEMICAL EQUATION

According to the law of conservation of mass, a balanced chemical equation has the same number of atoms of each element on both sides of the equation.

A chemical equation is balanced by *hit and trial method* or also called *trial and error method*.

A chemical equation is balanced as follows. For example, combustion of butane (C₄H₁₀).

Step 1. Write down the correct formulae of the reactants and products indicating the letter (g), (s), and (l) in the brackets next to its formula for gases, solids, and liquids, respectively, e.g.,



Step 2. Balance the number of C atoms: There are 4 C atoms in the reactant, therefore four CO₂ moles of CO₂ are required on the RHS of the equation.

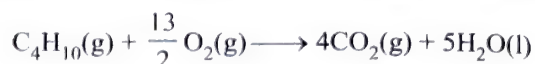


Step 3. Balance the number of H atoms: There are 10 H atoms in LHS in the reactants and each molecule of H₂O has 2H, atoms on RHS in the products, so 5 moles of H₂O are required for 10 H atoms on the RHS.



Step 4. Balance the number of O atoms: There are 13 O atoms on the RHS (4 × 2 = 8 in CO₂ and 5 × 1 = 5 in H₂O).

Therefore, 13/2 moles of O₂ are required on the LHS.



or



Step 5. Verify the number of atoms of each element is balanced in the final equation: The final equation shows 8 C, 20 H, and 26 O atoms on both side. Hence, the equation is balanced. Note that the subscripts in formulas of reactants and products are not changed to balance an equation.

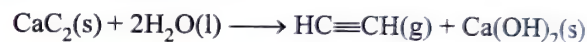
ILLUSTRATION 1.61

Calcium carbide reacts with water to give ethyne or acetylene gas and calcium hydroxide. Write the balanced chemical equation for this reaction.

Sol. The skeleton equation is



- Order of selection of atoms for balancing is O, H, and C.
- The number of O atoms on RHS is 2, and one O atom on LHS. So, multiply H₂O with 2.



It is a balanced chemical or atomic equation.

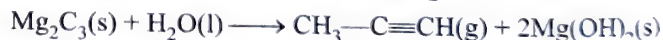
ILLUSTRATION 1.62

Magnesium carbide reacts with water to give propyne gas and magnesium hydroxide. Write the balanced chemical reaction.

Sol. The skeleton equation is:



- Order of selection of atoms for balancing Mg, O, H, and C.
- To equalise the number of Mg atoms on both sides, multiply the molecule of Mg(OH)₂ by 2.



- To equalise the number of O atoms on both sides, multiply the molecule of H₂O by 4.



It is a balanced chemical equation.

1.13 MOLE CONCEPT IN SOLUTIONS

The concentration of a solution or the amount of substance present in its given volume is expressed by the following terms:

- Molarity (M)
- Molality (m)
- Normality (N)
- Formality (F)
- Mole fraction (χ)
- Mass fraction (X)
- Mass percent or weight percent (W/W%)
- Parts per million (ppm)

1.13.1 MOLARITY

It is defined as the number of moles of solute in 1 L of the solution. It is the most widely used unit and is denoted by M . Thus,

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

Abbreviation used:

Symbol 1 or A is used for solvent and 2 or B is used for solute, e.g.,

Mass or weight of solvent = W_A or W_1

Mass or weight of solute = W_B or W_2

Moles of solvent = n_A or n_1

Moles of solute = n_B or n_2

Molar mass of solvent = Mw_A or Mw_1

Molar mass of solute = Mw_B or Mw_2

Mole fraction of solvent = χ_A or χ_1

Mole fraction of solute = χ_B or χ_2

Mass fraction of solvent = X_A or X_1

Mass fraction of solute = X_B or X_2

$$\text{Moles of solvent} = \frac{\text{Mass or weight of solvent}}{\text{Molar mass of solvent}} = \frac{W_1}{Mw_1}$$

$$\text{Moles of solute} = \frac{\text{Mass or weight of solute}}{\text{Molar mass of solute}} = \frac{W_2}{Mw_2}$$

$$\text{Formula of molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{n_2}{V_{\text{Sol}} \text{ (in L)}}$$

$$= \frac{W_2}{Mw_2 \times V_{\text{Sol}} \text{ (in L)}}$$

$$= \frac{W_2}{Mw_2 \times \frac{V_{\text{Sol}} \text{ (in mL)}}{1000}}$$

$$= \frac{W_2 \times 1000}{Mw_2 \times V_{\text{Sol}} \text{ (in mL)}}$$

Effect of temperature: Molarity of a solution depends upon temperature because volume of a solution is temperature dependent.

ILLUSTRATION 1.63

A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass percent of the solute.

Sol. Mass percent = $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$

$$= \frac{2 \text{ g}}{2 \text{ g} + 18 \text{ g}} \times 100$$

$$= 10\%$$

ILLUSTRATION 1.64

✓ Calculate the molarity of NaOH in solution prepared by dissolving 4 g in enough water to form 250 mL of the solution.

Sol. Molar mass (Mw_2) of solute (NaOH) = $(23 + 16 + 1) \text{ g} = 40 \text{ g}$

Use the formula of molarity

$$M = \frac{W_2 \times 1000}{Mw_2 \times V_{\text{Sol}} \text{ (in L)}} = \frac{4.0 \times 1000}{40 \times 250} = 0.4 \text{ mol L}^{-1} = 0.4 \text{ M}$$

1.13.2 MOLALITY

It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m .

$$\text{Formula of molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{n_2}{W_1 \text{ (in kg)}}$$

$$= \frac{W_2}{Mw_2 \times W_1 \text{ (in kg)}}$$

$$= \frac{W_2}{Mw_2 \times \frac{W_1 \text{ (in g)}}{1000}}$$

$$= \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

Mass or weight of solvent (W_1)

= Mass or weight of solution – Mass or weight of solute

Mass or weight of solution = $V_{\text{sol}} \times d_{\text{sol}}$

$$\therefore W_1 = (W_{\text{sol}} - W_2) = (V_{\text{sol}} \times d_{\text{sol}} - W_2)$$

$$\therefore m = \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

$$= \frac{W_2 \times 1000}{Mw_2 \times (V_{\text{sol}} \times d_{\text{sol}} - W_2)}$$

Effect of temperature: Molality of a solution does not change with temperature since mass remains unchanged with temperature.

Stock solution: The solution of a desired concentration is prepared by diluting a solution of known concentration. This solution of higher concentration is also known as *stock solution*.

Standard solution: A solution whose normality or molarity is known is called a *standard solution*.

• **Formula to convert molarity (M) to molality (m) and vice versa.**

$$d_{\text{sol}} = M \left(\frac{Mw_2}{1000} + \frac{1}{m} \right) \quad \dots(i)$$

To prove the relation, substitute the formula of M and m in Eq. (i).

$$\begin{aligned} d_{\text{sol}} &= \frac{W_2 \times 1000}{Mw_2 \times V_{\text{sol}}} \left(\frac{Mw_2}{1000} + \frac{Mw_2 \times W_1}{W_2 \times 1000} \right) \\ &= \frac{W_2}{V_{\text{sol}}} + \frac{W_1}{V_{\text{sol}}} \end{aligned}$$

$$= \frac{W_2 + W_1}{V_{\text{sol}}} = \frac{W_{\text{sol}}}{V_{\text{sol}}} = d_{\text{sol}}$$

Hence, LHS is equal to RHS, which proves the relation.

ILLUSTRATION 1.65

Calculate the molality of KCl solution prepared by dissolving 7.45 g of KCl in 500 mL of the solution. ($d_{\text{sol}} = 1.2 \text{ g mL}^{-1}$)

Sol. Molar mass of KCl = (39 + 35.5) g = 74.5 g

$$W_2 = 7.45 \text{ g}, M_{w_2} = 74.5 \text{ g}$$

$$V_{\text{sol}} = 500 \text{ mL}$$

$$d_{\text{sol}} = 1.2 \text{ g mL}^{-1}$$

$$m = \frac{W_2 \times 1000}{M_{w_2} \times W_1}$$

In the above relation, W_1 is unknown, so find W_1 .

$$W_1 = (W_{\text{sol}} - W_2) \text{ g} = (V_{\text{sol}} \times d_{\text{sol}} - W_2) \text{ g}$$

$$= (500 \times 1.2 - 7.45) \text{ g} = 592.55 \text{ g}$$

$$\therefore m = \frac{7.45 \times 1000}{74.5 \times 592.55} = 0.168 \text{ m}$$

ILLUSTRATION 1.66

Calculate the molality (m) of 3M solution of NaCl whose density is 1.25 g mL^{-1} .

Sol. Molar mass (M_{w_2}) of NaCl = (23 + 35.5) g = 58.5 g

$$M = 3 \text{ mol L}^{-1}$$

Mass or weight (W_2) of NaCl in 1 L solution

$$= 3 \times 58.5 = 175.5 \text{ g}$$

First method:

Use direct relation:

$$d_{\text{sol}} = M \left(\frac{M_{w_2}}{1000} + \frac{1}{m} \right)$$

$$1.25 \text{ g mL}^{-1} = 3 \left(\frac{58.5}{1000} + \frac{1}{m} \right)$$

$$\frac{1.25}{3} - \frac{58.5}{1000} = \frac{1}{m}$$

$$0.416 - 0.058 = \frac{1}{m}$$

$$0.358 = \frac{1}{m}$$

$$m = \frac{1}{0.358} = 2.79 \text{ m}$$

Second method:

$$M = 3 \text{ mol L}^{-1}$$

Mass of NaCl in 1 L solution (W_2) = $3 \times 58.5 = 175.5 \text{ g}$

$$\text{Mass of 1 L solution} = V_{\text{sol}} \times d_{\text{sol}}$$

$$= 1000 \times 1.25 = 1250 \text{ g}$$

Mass of H_2O in solution (W_1)

$$= \text{Mass of solution} - \text{Mass of solute}$$

$$= W_{\text{sol}} - W_2$$

$$= 1.250 - 0.1755 = 1.0745 \text{ kg}$$

$$\therefore m = \frac{W_2 \times 1000}{M_{w_2} \times W_1}$$

$$= \frac{175.5 \times 1000}{58.5 \times 1074.5} = 2.79 \text{ m}$$

$$\text{or } m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{3 \text{ mol}}{1.0745 \text{ kg}} = 2.79 \text{ m}$$

1.13.3 NORMALITY

It is defined as the number of gram equivalents of the solute in 1 L of the solution and is denoted by N . Thus,

$$\text{Normality (N)} = \frac{\text{Number of gram equivalent of the solute}}{\text{Volume of solution in litres}}$$

$$\text{Gram equivalent} = \frac{\text{Mass of solute (} W_2 \text{)}}{\text{Equivalent mass of the solute (} E_{w_2} \text{)}}$$

Equivalent mass (or weight) of solute

$$= \frac{\text{Molar mass of the solute (} M_{w_2} \text{)}}{n}$$

where n is the basicity of an acid or acidity of a base or total positive or negative charge of an ionic compound or number of electrons involved in a redox reaction (called n factor or valency factor)

Basicity of an acid: It is the number of replaceable H^+ ion.

For example,

HCl is monobasic acid, $n = 1$, one H^+ ion is replaceable.

H_2SO_4 is dibasic acid, $n = 2$, two H^+ ions are replaceable.

H_3PO_4 (phosphoric acid) is tribasic acid, $n = 3$, three H^+ ions are replaceable. H_3PO_3 (phosphorous or phosphonic acid)

$\left(\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{P}-\text{OH} \\ | \\ \text{OH} \end{array} \right)$ is dibasic acid, $n = 2$, two H^+ ions are replaceable.

H_3PO_2 (hypophosphorous or phosphinic acid) $\left(\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{P}-\text{OH} \\ | \\ \text{H} \end{array} \right)$ is

monobasic acid, $n = 1$, one H^+ ion is replaceable.

Acidity of a base: It is the number of replaceable OH^- ions.

For example,

NaOH is monoacidic base, $n = 1$, one OH^- ion is replaceable.

Ca(OH)_2 is diacidic base, $n = 2$, two OH^- ions are replaceable.

Al(OH)_3 is triacidic base, $n = 3$, three OH^- ions are replaceable.

n factor of salt: It is the total positive or negative charge. For example,

$\oplus \ominus$
NaCl, $n = 1$, one positive or negative charge

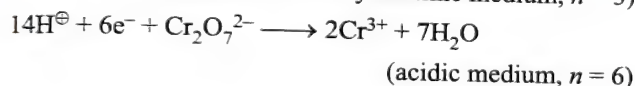
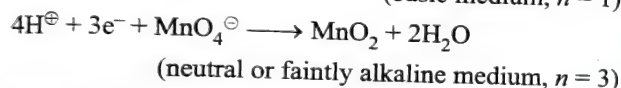
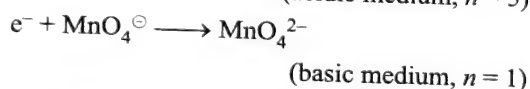
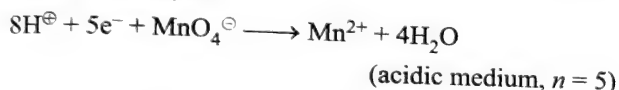
$+2 -1 \times 2$
BaCl₂, $n = 2$, two positive or negative charge

$+2 -2$
FeC₂O₄, (ferrous oxalate), $n = 2$, two positive or negative charge

$+2 \times 3 -2 \times 3$
Fe₂(C₂O₄)₃, (ferric oxalate), $n = 6$, six positive or negative charge

$+2 -2 +1 \times 2 -2$
FeSO₄(NH₄)SO₄·6H₂O (Mohr's salt), $n = 6$, six positive or negative charge

n factor of a redox reaction: It is the number of electrons involved in a reduction or oxidation (redox) reaction (refer Chapter 2 for details). For example,



Formulae of Normality (N)

$$N = \frac{\text{Number of gram equivalent of the solute}}{\text{Volume of solution in litres}}$$

$$= \frac{W_2}{E_{w_2} \times V_{\text{sol}} \text{ (in L)}} = \frac{W_2}{E_{w_2} \times \frac{V_{\text{sol}} \text{ in mL}}{1000}}$$

$$= \frac{W_2 \times 1000}{E_{w_2} \times V_{\text{sol}} \text{ in mL}} = \frac{W_2 \times 1000}{\frac{M_{w_2}}{n} \times V_{\text{sol}} \text{ (in mL)}}$$

$$= n \times \frac{W_2 \times 1000}{M_{w_2} \times V_{\text{sol}} \text{ (in mL)}} = n \times M$$

Thus, $N = n \times M$.

Note: N = Number of gram equivalent L⁻¹

= Number of milliequivalent mL⁻¹

M = Number of moles L⁻¹

= Number of millimoles mL⁻¹

$N \times V \text{ (L)} = \text{Gram equivalent or simply equivalent}$

$N \times V \text{ (mL)} = \text{Milliequivalent}$

$M \times V \text{ (L)} = \text{Moles}$

$M \times V \text{ (mL)} = \text{Millimoles}$

Normality equations: If a solution having normality N_1 and volume V_1 is diluted to volume V_2 , so that the new normality is N_2 , then the number of gram equivalent remains the same in the solution. Thus,

$$N_1 \times V_1 = N_2 \times V_2$$

This equation is called **normality equation**.

If solutions having normalities N_1, N_2, N_3, \dots and volumes V_1, V_2, V_3, \dots , respectively, are mixed together then the normality (N_n) of final resulting solution is:

$$N_1 V_1 + N_2 V_2 + N_3 V_3 + \dots = N_n V_n$$

$$(V_n = V_1 + V_2 + V_3 + \dots)$$

Molarity equation: If a solution with molarity M_1 and volume V_1 is diluted to volume V_2 , so that the new molarity is M_2 , then as the number of moles remains same in the solution. Thus,

$$M_1 \times V_1 = M_2 \times V_2$$

This equation is called **molarity equation**.

For the neutralisation of V_1 mL of an acid with molarity M_1 and basicity n_a by V_2 mL of a base with molarity M_2 and acidity n_b ,

$$n_a M_1 V_1 = n_b M_2 V_2$$

When two reactants A and B , with n_A and n_B moles react, then,

$$\frac{M_A V_A}{n_A} = \frac{M_B V_B}{n_B}$$

ILLUSTRATION 1.67

Calculate the molarity (M) and normality (N) of a solution of oxalic acid [(COOH)₂·2H₂O] containing 12.6 g of the acid in 500 mL of the solution.

Sol. Molar mass of (COOH)₂·2H₂O = 2(12 + 32 + 1) + 2(18)

$$= 90 + 36 = 126 \text{ g}$$

$$\text{Equivalent mass of (COOH)}_2 \cdot 2\text{H}_2\text{O} = \frac{\text{Molar mass}}{n}$$

$$= \frac{126}{2} = 63 \text{ g}$$

($n = 2$, since two H[⊕] ions are replaceable, i.e., dibasic acid)

$$M = \frac{W_2 \times 1000}{M_{w_2} \times V_{\text{sol}} \text{ (in mL)}} = \frac{12.6 \times 1000}{126 \times 500} = 0.02 \text{ M}$$

$$N = \frac{W_2 \times 1000}{E_{w_2} \times V_{\text{sol}} \text{ (in mL)}} = \frac{12.6 \times 1000}{63 \times 500} = 0.4 \text{ N}$$

(Alternatively, $N = n \times M = 2 \times 0.2 = 0.4 \text{ N}$)

ILLUSTRATION 1.68

100 mL of 0.1 M HCl + 100 mL of 0.2 M H₂SO₄ + 100 mL of 0.1 M HNO₃ are mixed together.

- What is the final concentration of the solution?
- What would be the final concentration of the solution, if the solution is made to 1 L by adding H₂O?
- What would be the final concentration of the solution if 700 mL of H₂O is added to the solution?

Sol.

$$a. N_1 V_1 + N_2 V_2 + N_3 V_3 = N_4 V_4$$

$$(V_4 = V_1 + V_2 + V_3 = 100 + 100 + 100 = 300 \text{ mL})$$

n factor for HCl and HNO₃ = 1

n factor for $\text{H}_2\text{SO}_4 = 2$

In such questions always convert molarity to normality, since 1 gram equivalent of one reactant is always equal to 1 gram equivalent of another reactant.

$$100 \times 0.1 + 100 \times 0.2 \times 2 + 100 \times 0.1 = N_4 \times 300$$

$$10 + 40 + 10 = N_4 \times 300$$

$$\therefore N_4 = \frac{60}{300} = \frac{1}{5} = 0.2 \text{ N}$$

Hence, final concentration of solution = 0.2 N

b. Final volume = 1 L = 1000 mL

$$\therefore 100 \times 0.1 + 100 \times 0.2 \times 2 + 100 \times 0.1 = N_4 \times 1000$$

$$N_4 = \frac{60}{1000} = 0.06 \text{ N}$$

Hence, final concentration of solution = 0.06 N

c. Final volume = 300 + 700 = 1000 mL

$$\therefore N_4 = \frac{60}{1000} = 0.06 \text{ N}$$

Hence, final concentration of solution = 0.06 N

ILLUSTRATION 1.69

1 L of 0.1 M NaOH, 1 L of 0.2 M KOH, and 2 L of 0.05 M $\text{Ba}(\text{OH})_2$ are mixed together. What is the final concentration of the solution.

Sol. Total volume (V_4) = 1 + 1 + 2 = 4 L

n factor for NaOH and KOH is 1, while for $\text{Ba}(\text{OH})_2$ is 2.

$$N_1 V_1 + N_2 V_2 + N_3 V_3 = N_4 V_4$$

$$0.1 \times 1 + 0.2 \times 1 + 0.05 \times 2 \times 2 = N_4 \times 4$$

$$0.1 + 0.2 + 0.2 = N_4 \times 4$$

$$N_4 = \frac{0.4}{4} = 0.1 \text{ N}$$

Hence, final concentration of solution = 0.1 N

ILLUSTRATION 1.70

✓ 50 mL of 0.2 M HCl, 50 mL of 0.2 NH_4SO_4 , and 200 mL of 0.2 M $\text{Ba}(\text{OH})_2$ are mixed together and the volume was made to 1 L by adding H_2O . What is the final concentration of the solution, and what is the nature of the final solution: acidic, basic or neutral?

Sol. In this case, strong acids and strong bases are mixed. Equal amount of milli equivalents of acid and base will neutralise. Concentrations of HCl and $\text{Ba}(\text{OH})_2$ are in molarities; they have to be converted to normalities as concentration of H_2SO_4 is given in normality.

$$\therefore \text{Total acids} = 50 \times 0.2 \times 1 + 50 \times 0.2 \times 1$$

$$10 + 10 = 20 \text{ mEq}$$

$$\begin{aligned} \text{Total base} &= 200 \times 0.2 \times 2 \text{ (} n \text{ factor)} \\ &= 80 \text{ mEq} \end{aligned}$$

Since 20 mEq of acid would neutralise 20 mEq of base, thus,

$$\text{Base left} = 80 - 20 = 60 \text{ mEq}$$

$$\text{Total volume of solution} = 1 \text{ L} = 1000 \text{ mL}$$

$$\text{So, final concentration of solution} = \frac{\text{mEq}}{\text{mL}} = \frac{60}{1000} = 0.06 \text{ N}$$

Final resulting mixture of solution is basic, since 60 mEq of strong base is left.

1.13.4 FORMALITY

It is used to express the concentration of the solutions of ionic compounds (since they are not molecular) in place of molarity.

Since the molar mass or the molecular weight of ionic solids is not determined accurately experimentally due to their dissociation nature, therefore, the molecular weight of ionic solid is often referred as formula weight and molarity as formality.

It is defined as the number of formula weights present in 1 L of the solution.

$$\begin{aligned} \text{Formality} &= \frac{\text{Mass or weight of the compound in gram}}{\text{Formula weight of the compound in gram} \times \text{Volume of solution in litre}} \\ &= \frac{W_2 \times 1000}{\text{Formula weight of the compound} \times V_{\text{sol}} \text{ (in mL)}} \end{aligned}$$

Like molarity, formality is temperature dependent.

1.13.5 MOLE FRACTION (χ)

It is the ratio of number of moles of a particular component to the number of moles of the solution. It is denoted by the symbol χ (called chi). If solute B dissolves in solvent A and their number of moles are n_B and n_A , respectively, then their mole fraction χ_A and χ_B are given as:

$$\text{Mole fraction of solvent A} = \chi_A$$

$$\begin{aligned} &= \frac{\text{Number of moles of A}}{\text{Number of moles of solution}} \\ &= \frac{n_A}{n_A + n_B} = \frac{W_A / M_{w_A}}{W_A / M_{w_A} + W_B / M_{w_B}} \end{aligned}$$

$$\text{Mole fraction of solute B} = \chi_B$$

$$\begin{aligned} &= \frac{\text{Number of moles of B}}{\text{Number of moles of solution}} \\ &= \frac{n_B}{n_A + n_B} = \frac{W_B / M_{w_B}}{W_A / M_{w_A} + W_B / M_{w_B}} \end{aligned}$$

Since total mole fractions of solute and solvent (i.e., solution) is 1.

$$\therefore \chi_A + \chi_B = 1$$

$$\chi_B = 1 - \chi_A$$

If two solutes are dissolved in solvent. Let the number of moles of solvent and the two solutes are n_1 , n_2 , and n_3 , respectively, then,

$$\text{Mole fraction of solvent } (\chi_1) = \frac{n_1}{n_1 + n_2 + n_3}$$

$$= \frac{W_1 / M_{w_1}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}} + \frac{W_3}{M_{w_3}}}$$

$$\text{Mole fraction of first solute } (\chi_2) = \frac{n_2}{n_1 + n_2 + n_3}$$

$$= \frac{W_2 / M_{w_2}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}} + \frac{W_3}{M_{w_3}}}$$

$$\text{Mole fraction of second solute } (\chi_3) = [1 - (\chi_1 + \chi_2)] \text{ or}$$

$$= \frac{n_3}{n_1 + n_2 + n_3}$$

$$= \frac{W_3 / M_{w_3}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}} + \frac{W_3}{M_{w_3}}}$$

ILLUSTRATION 1.71

A solution contains 2.5 mol of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and 7.5 mol of H_2O . Calculate the mole fraction of each component of the solution.

$$\text{Sol. } \chi_{\text{ethanol}} = \frac{n_2}{n_1 + n_2} = \frac{2.5}{2.5 + 7.5} = \frac{2.5}{10} = 0.25$$

$$\chi_{\text{H}_2\text{O}} = 1 - 0.25 = 0.75$$

ILLUSTRATION 1.72

The percentage composition by mass of a solution is 20% urea (NH_2CONH_2), 40% glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), and 40% water (H_2O). Calculate the mole fraction of each component of the solution.

$$\text{Sol. Molar mass of urea } (\text{NH}_2\text{CONH}_2) (M_{w_2})$$

$$= (\text{NH}_2)_2\text{CO}$$

$$= 2(14 + 2) + 12 + 16$$

$$= 32 + 12 + 16 = 60 \text{ g mol}^{-1}$$

$$\text{Molar mass of glucose } (\text{C}_6\text{H}_{12}\text{O}_6) (M_{w_3})$$

$$= 12 \times 6 + 12 + 6 \times 16$$

$$= 72 + 12 + 96 = 180 \text{ g mol}^{-1}$$

$$\text{Molar mass of } \text{H}_2\text{O} (M_{w_1}) = 18 \text{ g mol}^{-1}$$

$$\chi_{\text{urea}} (\chi_2) = \frac{n_2}{n_1 + n_2 + n_3} = \frac{W_2 / M_{w_2}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}} + \frac{W_3}{M_{w_3}}}$$

$$= \frac{20 / 60}{\frac{40}{18} + \frac{20}{60} + \frac{40}{180}}$$

$$= \frac{0.33}{2.2 + 0.33 + 0.22}$$

$$= \frac{0.33}{2.75} = 0.12$$

$$\chi_{\text{glucose}} (\chi_3) = \frac{n_3}{n_1 + n_2 + n_3} = \frac{W_3 / M_{w_3}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}} + \frac{W_3}{M_{w_3}}}$$

$$= \frac{40 / 180}{2.2 + 0.33 + 0.22}$$

$$= \frac{0.22}{2.2 + 0.33 + 0.22}$$

$$= \frac{0.22}{2.75} = 0.08$$

$$\chi_{\text{H}_2\text{O}} (\chi_1) = [1 - (\chi_2 + \chi_3)] = [1 - (0.12 + 0.08)] = 0.8$$

$$\text{Hence, } \chi_1 = 0.8, \chi_2 = 0.12, \chi_3 = 0.08$$

Relation Between Molality (m) and Moles and Mole Fraction

The formula of molality (m) is

$$m = \frac{W_2 \times 1000}{M_{w_2} \times W_1}$$

$$= \frac{W_2 \times 1000}{M_{w_2} \times \frac{W_1}{M_{w_1}} \times M_{w_1}} \quad \left(\frac{W_2}{M_{w_2}} = n_2, \frac{W_1}{M_{w_1}} = n_1 \right)$$

$$= \frac{n_2 \times 1000}{n_1 \times M_{w_1}} = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}} \quad \left(\text{Since } \frac{\chi_2}{\chi_1} = \frac{\frac{n_2}{n_1 + n_2}}{\frac{n_1}{n_1 + n_2}} = \frac{n_2}{n_1} \right)$$

$$\text{Thus, } m = \frac{n_2 \times 1000}{n_1 \times M_{w_1}} = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}}$$

Note: In case of a solution of two liquid solution, the liquid with more amount of moles or mole fraction is taken as solvent and the liquid with less amount or moles or mole fraction is taken as solute. For example, refer Illustration 1.73.

ILLUSTRATION 1.73

A solution is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

- What is the molality (m) of the solution?
- Water is added to the above solution such that the mole fraction of water in the solution becomes 0.9. What is the molality (m) of the solution?

Sol.

$$\text{a. Molar mass of } \text{H}_2\text{O} = 18 \text{ g mol}^{-1}$$

$$\text{Molar mass of ethanol } (\text{C}_2\text{H}_5\text{OH})$$

$$= 2 \times 12 + 5 + 16 + 1$$

$$= 46 \text{ g mol}^{-1}$$

Mole fraction of ethanol is 0.9 and is greater than the mole fraction of water (i.e., $1 - 0.9 = 0.1$), so ethanol is solvent and water is solute. Thus, $\chi_1 = 0.9$ and $\chi_2 = 0.1$ ($M_{w_1} = 46$ and $M_{w_2} = 18$).

$$\therefore m = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}} = \frac{\text{Mole fraction of solute} \times 1000}{\text{Mole fraction of solvent} \times \text{Molar mass of solvent}}$$

$$= \frac{0.1 \times 1000}{0.9 \times 46} = 2.415 \text{ m}$$

- b. Now mole fraction of water is 0.9 and is greater than the mole fraction of ethanol (i.e., $1 - 0.9 = 0.1$), so **water is solvent** and **ethanol is solute**. Thus, $\chi_1 = 0.9$, $\chi_2 = 0.1$ ($M_{w_1} = 18$ and $M_{w_2} = 46$).

$$\therefore m = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}} = \frac{0.1 \times 1000}{0.9 \times 18} = 6.17 \text{ m}$$

1.13.6 MASS FRACTION (X)

It is the ratio of mass of a particular component to the total mass of the solution. It is denoted by symbol (X). If a solute B of mass or weight of W_2 is dissolved in a solvent A of mass or weight of W_1 , then the mass fraction of solvent (X_1) and solute (X_2) are given as

$$\text{Mass fraction of solvent } A (X_1) = \frac{W_1}{W_1 + W_2}$$

$$\text{Mass fraction of solute } B (X_2) = \frac{W_2}{W_1 + W_2}$$

$$\text{or } X_2 = 1 - X_1$$

1.13.7 PERCENT CONCENTRATIONS

a. Mass percent or weight percent ($W/W\%$) or ($W_2/W_{\text{sol}}\%$)

It is defined as the mass of solute dissolved in 100 g or 100 kg of solution. It is denoted by ($W_2/W_{\text{sol}}\%$).

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100 = \frac{W_2 \times 100}{W_{\text{sol}}}$$

For example, an aqueous solution of H_2SO_4 is 49% by weight or by mass or simply 49% it is taken as mass percent. It means 49 g of H_2SO_4 is dissolved in 100 g of solution.

Formula for molarity (M) when mass percent is given

$$M = \frac{W_2 \times 1000}{M_{w_2} \times V_{\text{sol}} \text{ (in mL)}}$$

$$= \frac{W_2 \times 1000}{M_{w_2} \times \frac{\text{Mass or weight of solution}}{\text{Density of solution}}} \left(\frac{\text{Mass}}{\text{Volume}} = d \right)$$

$$= \frac{W_2 \times 1000 \times d_{\text{sol}}}{M_{w_2} \times W_{\text{sol}}}$$

$$= \frac{W_2 \times 1000 \times d_{\text{sol}}}{M_{w_2} \times 100}$$

$$= \frac{W_2 \times 10 \times d_{\text{sol}}}{M_{w_2}} = \frac{\% \text{ by mass} \times 10 \times d_{\text{sol}}}{M_{w_2}}$$

For example, 49% by mass or weight of aqueous solution of H_2SO_4 , whose density of solution is 1.1 g mL^{-1} .

The molarity (M) is:

$$\text{Molar mass of } \text{H}_2\text{SO}_4 = 2 + 32 + 16 \times 4 = 98 \text{ g mol}^{-1}$$

$$M = \frac{\% \text{ by mass} \times 10 \times d_{\text{sol}}}{M_{w_2}} = \frac{49 \times 10 \times 1.1}{98}$$

$$= 5.5 \text{ mol L}^{-1} = 5.5 \text{ M}$$

b. Volume percent ($V/V\%$ or $V_2/V_{\text{sol}}\%$)

It is defined as the volume of solute dissolved in 100 mL or 100 L of solution. It is denoted by ($V_2/V_{\text{sol}}\%$).

$$\text{Volume percent} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100 = \frac{V_2 \times 100}{V_{\text{sol}}}$$

For example, if aqueous solution of ethanol is 46% by volume, it means 46 mL of ethanol is dissolved in 100 mL of solution.

c. Mass by volume percent ($W/V\%$ or $W_2/V_{\text{sol}}\%$)

It is defined as the mass or weight of solute dissolved in 100 g or 100 kg of solution. It is denoted by ($W_2/V_{\text{sol}}\%$).

$$\text{Mass/volume percent} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

$$= \frac{W_2 \times 100}{V_{\text{sol}}}$$

For example, a solution of glucose is 18% by mass/volume, it means 18 g of glucose is dissolved 100 mL of solution.

d. Volume by mass percent ($V/W\%$ or $V_2/W_{\text{sol}}\%$)

It is defined as the volume of solute dissolved in 100 g or 100 kg of solution. It is denoted by ($V_2/W_{\text{sol}}\%$).

$$\text{Volume/mass percent} = \frac{\text{Volume of solute}}{\text{Mass of solution}} \times 100$$

$$= \frac{V_2 \times 100}{W_{\text{sol}}}$$

For example, aqueous solution of ethanol is 46% by volume/mass. It means 46 mL or 46 L of ethanol is dissolved in 100 g or 100 kg of solution.

ILLUSTRATION 1.74

- ✓ Calculate the molarity (M) and molality (m) of 16% aqueous methanol (CH_3OH) solution by volume. Density of solution = 0.9 g mL^{-1} .

Sol. 16 mL of CH_3OH is dissolved in 100 mL of solution.

$$\text{Volume and mass of } \text{H}_2\text{O} = 100 - 16 = 84 \text{ mL} = 84 \text{ g}$$

$$\text{(since } d_{\text{H}_2\text{O}} = 1 \text{ g mL}^{-1}\text{)}$$

$$\text{Mass of solution} = V_{\text{sol}} \times d_{\text{sol}}$$

$$= 100 \times 0.9 = 90 \text{ g}$$

$$\text{Mass or weight of solute } (W_2) = W_{\text{sol}} - W_1$$

$$= 90 - 84 = 6 \text{ g}$$

$$\text{Molar mass of } \text{CH}_3\text{OH} = 32 \text{ g}$$

$$\therefore M = \frac{W_2 \times 1000}{M_{w_2} \times V_{\text{sol}}} = \frac{6 \times 1000}{32 \times 100} = 1.875 \text{ M}$$

$$m = \frac{W_2 \times 1000}{M_{w_2} \times W_1} = \frac{6 \times 1000}{32 \times 84} = 2.232 \text{ m}$$

1.13.8 PARTS PER MILLION (PPM)

It is defined as the mass of solute dissolved in 1 millionth part (10^6) of the mass of solution. It is denoted by ppm. Thus,

$$\text{ppm} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}} = \frac{W_2 \times 10^6}{W_{\text{sol}}}$$

ILLUSTRATION 1.75

20 mg of K^{\oplus} ions are present in 1 L of aqueous solution. Density of the solution is 0.8 g mL^{-1} . What is the concentration of K^{\oplus} ions in ppm?

Sol. Mass of K^{\oplus} ions (W_2) = 20 mg = $20 \times 10^{-3} \text{ g}$

Mass of solution = $V_{\text{sol}} \times d_{\text{sol}} = 1000 \text{ mL} \times 0.8 \text{ g mL}^{-1} = 800 \text{ g}$

$$\text{ppm} = \frac{W_2 \times 10^6}{W_{\text{sol}}} = \frac{20 \times 10^{-3} \times 10^6}{800} = 25 \text{ ppm}$$

1.14 HARDNESS OF WATER

- The hardness of water is due to the presence of bicarbonates, chlorides, and sulphates of Ca and Mg.
- The hardness is temporary due to bicarbonates and permanent due to chlorides and sulphates of Ca and Mg.
- The extent of hardness is known as the degree of hardness defined as the number of parts by weight of CaCO_3 present per million parts by weight of water.

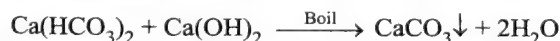
$$\text{Hardness} = \frac{\text{Grams of } \text{CaCO}_3}{10^6 \text{ g of water}} = \frac{\text{Grams of } \text{CaCO}_3}{10^6 \text{ mL of water}} \quad (\because d = 1)$$

Water softness: The hardness may be removed by either of the reactants on treating with water.

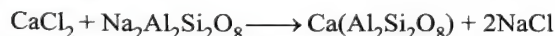
a. Washing soda:



b. Slaked lime:



c. Permutit or sodium aluminium orthosilicate or sodium zeolite:



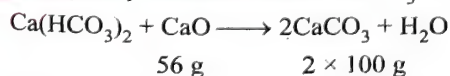
d. Calgon or sodium hexametaphosphate:



ILLUSTRATION 1.76

10 L of hard water requires 0.28 g of lime (CaO) for removing hardness. Calculate the temporary hardness in ppm of CaCO_3 .

Sol. Temporary hardness is due to HCO_3^{\ominus} of Ca^{2+} and Mg^{2+} .



56 g CaO = 200 g CaCO_3 in 10 L of H_2O

$$0.28 \text{ g } \text{CaO} = \frac{200 \times 0.28}{56}$$

$$= 1 \text{ g } \text{CaCO}_3 \text{ in } 10 \text{ L of } \text{H}_2\text{O}$$

$$= 1 \text{ g } \text{CaCO}_3 \text{ in } 10 \times 1000 \text{ mL of } \text{H}_2\text{O}$$

$$= 1 \text{ g } \text{CaCO}_3 \text{ in } 10^4 \text{ mL of } \text{H}_2\text{O}$$

$$= 100 \text{ g } \text{CaCO}_3 \text{ in } 10^6 \text{ mL of } \text{H}_2\text{O} = 100 \text{ ppm}$$

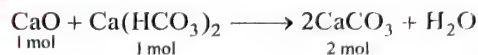
Hence, temporary hardness of CaCO_3 = 100 ppm.

ILLUSTRATION 1.77

Calculate the weight of CaO required to remove hardness of 10^6 L of water containing 1.62 g of $\text{Ca}(\text{HCO}_3)_2$ in 1.0 L.

(M_w of $\text{Ca}(\text{HCO}_3)_2$ = 162, M_w of CaO = 56)

Sol. The reaction is:



$$\text{Moles of } \text{Ca}(\text{HCO}_3)_2 \text{ in } 1.0 \text{ L of sample} = \frac{1.62}{162} = 0.01 \text{ mol}$$

$$\text{Moles of } \text{CaO} \text{ required in } 1.0 \text{ L of sample} = 0.01 \text{ mol L}^{-1}$$

$$\text{Moles of } \text{CaO} \text{ required in } 10^6 \text{ L of sample}$$

$$= 0.01 \times 10^6 \text{ mol} / 10^6 \text{ L} = 10^4 \text{ mol } (10^6 \text{ L})^{-1}$$

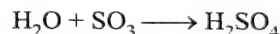
$$\text{Weight of } \text{CaO} = 10^4 \times 56 = 5.6 \times 10^5 \text{ g}$$

1.15 PERCENT FREE SO_3 IN AN OLEUM

What is percent free SO_3 in an oleum (considered as a solution of SO_3 in H_2SO_4) that is labelled '109% H_2SO_4 '? Such a designation refers to the total mass of pure H_2SO_4 , 109 g, that would be present after dilution of 100 g of the oleum, when all free SO_3 would combine with water to form H_2SO_4 .

9 g H_2O will combine with all the free SO_3 in 100 g of the oleum to give a total of 109 g H_2SO_4 .

The equation



indicates that 1 mole H_2O (18 g) combines with 1 mol SO_3 (80 g). Then, 9 g H_2O combines with

$$= \frac{9 \times 80}{18} = 40 \text{ g } \text{SO}_3$$

Thus, 100 g of the oleum contains 40 g SO_3 or the percent free in the oleum is 40%.

Using the above result,

$$109 = \left(100 + \frac{18x}{80} \right) \%$$

$$x = 40\%$$

ILLUSTRATION 1.78

Calculate the percent free SO_3 in an oleum which is labelled '118% H_2SO_4 '.

Sol. $(118 - 100) = 18 \text{ g } \text{H}_2\text{O}$ combine with all the free SO_3 in 100 g of the oleum to give a total of 118 g H_2SO_4 .
18 g H_2O combines with 80 g SO_3 .

$$\text{Thus, percent free } \text{SO}_3 \text{ in the oleum} = \frac{18 \times 80}{18} = 80\%$$

ILLUSTRATION 1.79

If the percent free SO_3 in an oleum is 20%, then label the sample of oleum in terms of percent H_2SO_4 .

Sol. Let $x \text{ g } \text{H}_2\text{O}$ combines with all the free SO_3 in 100 g of the oleum to give a total $(100 + x) \text{ g } \text{H}_2\text{SO}_4$.

18 g H₂O combines with 80 g SO₃

$$x \text{ g H}_2\text{O combines with} = \frac{x}{18} \times 80 = 20 \text{ g SO}_3$$

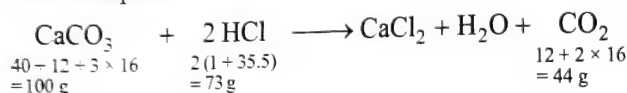
$$\therefore x = \frac{20 \times 18}{80} = 4.5 \text{ g}$$

$$\begin{aligned} \text{Labelling of oleum in terms of percent H}_2\text{SO}_4 \\ = (100 + x) = (100 + 4.5) = 104.5\% \text{ H}_2\text{SO}_4 \end{aligned}$$

1.16 LIMITING REAGENT

Sometimes, one of the reactants is not present in the amounts as required by a balanced chemical reaction and is in the excess amount over the other. The reactant which is present in the lesser amount is consumed after some time and after that no further reaction takes place whatever be the amount of the other reactant present. Hence, the reactant, which is completely consumed, limits the amount of the product formed and is therefore called the *limiting reagent*.

For example.



According to the balanced chemical reaction, 100 g CaCO₃ reacts with 73 g of HCl to give 44 g of CO₂.

Example: If 10.0 g of CaCO₃ is reacted with 10.0 g of HCl, what mass of CO₂ will be produced and which reactant is the limiting reagent?

100 g CaCO₃ requires 73 g HCl.

10 g CaCO₃ requires 7.3 g HCl.

Mass of HCl left unreacted 10 - 7.3 = 2.7 g

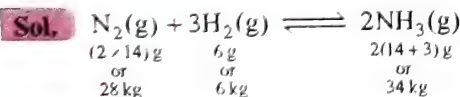
Hence, CaCO₃ is the limiting reagent, since it is completely consumed in the reaction and CaCO₃ will decide the amount of product formed.

100 g CaCO₃ gives 44 g CO₂.

10 g CaCO₃ gives 4.4 g CO₂.

ILLUSTRATION 1.80

50.0 kg of N₂(g) and 10.0 kg of H₂(g) are mixed to produce NH₃(g). Calculate the NH₃(g) formed. Identify the limiting reagent.



According to the balanced chemical reaction, 28 kg of N₂ reacts with 6 kg of H₂ to give 34 kg of NH₃.

Thus, 6 kg of H₂ requires 28 kg of N₂.

$$10 \text{ kg of H}_2 \text{ requires } \frac{28 \times 10}{6} = 46.6 \text{ kg of N}_2.$$

Hence, H₂ is the limiting reagent, since it is completely consumed in the reaction, and H₂ will decide the amount of product formed.

Thus, 6 kg of H₂ \equiv 34 kg of NH₃

$$10 \text{ kg of H}_2 \equiv \frac{34 \times 10}{6} = 56.6 \text{ kg of NH}_3$$

ILLUSTRATION 1.81

If 0.5 mol of CaBr₂ is mixed with 0.2 mol of K₃PO₄, the maximum number of moles of Ca₃(PO₄)₂ that can be formed is:

- a. 0.1 b. 0.2 c. 0.5 d. 0.7

Sol.



According to the chemical reaction,

2 mol of K₃PO₄ reacts = 3 mol of CaBr₂

0.2 mol. of K₃PO₄ reacts = 0.3 mol of CaBr₂

Moles of CaBr₂ left unreacted = 0.5 - 0.3 = 0.2

Hence, K₃PO₄ is the limiting reagent, since it reacts completely and it decides the amount of products, thus formed.

2 mol of K₃PO₄ gives 1 mol of Ca₃(PO₄)₂.

0.2 mol of K₃PO₄ gives = 0.1 mol of Ca₃(PO₄)₂.

Thus, the answer is (a).

ILLUSTRATION 1.82

Upon mixing 100.0 mL of 0.1 M potassium sulphate solution and 100.0 mL of 0.05 M barium chloride solution, precipitation of barium sulphate takes place. How many moles of barium sulphate are formed? Also, calculate the molar concentration of species left behind in the solution. Which is the limiting reagent?

Sol.

	$\text{K}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow \text{BaSO}_4 \downarrow + 2 \text{KCl}$			
(According to equation)	1 mmol	1 mmol	1 mmol	2 mmol
(mmole before reaction)	100 × 0.1 = 10 mmol	100 × 0.05 = 5 mmol	—	—
(mmole left after reaction)	10 - 5 = 5 mmol	—	5 mmol	10 mmol

5 mmol of BaCl₂ will react with 5 mmol of K₂SO₄. Hence BaCl₂ is the limiting reagent which is completely consumed in the reaction and it will decide the number of millimoles of products formed.

Total volume of solution = 100 + 100 = 200 mL

Moles of BaSO₄ precipitated = $\frac{5 \text{ mmol}}{1000 \text{ mL}} = 0.005 \text{ mol}$

Unreacted K₂SO₄ and KCl are left in the solution.

Concentration of K₂SO₄ left in the solution = $\frac{5 \text{ mmol}}{200 \text{ mL}} = 0.025 \text{ M}$

Concentration of KCl formed in the reaction = $\frac{10 \text{ mmol}}{200 \text{ mL}} = 0.05 \text{ M}$

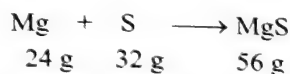
1.17 PERCENT YIELD

The experimental yield or actual yield in any reaction is always less than the theoretical or calculated yield from the balanced chemical reaction. This is because of certain side reactions taking place or less ideal conditions then required.

Therefore, percent yield is the percent ratio of experiment and theoretical yield.

$$\text{Percent yield} = \frac{\text{Experimental yield}}{\text{Calculated yield}} \times 100$$

For example,



The calculated yield of MgS in the above reaction is 56 g, but experimentally it was observed to be 50 g

$$\text{Hence, percent yield} = \frac{50 \times 100}{56} = 89.28\%$$

CONCEPT APPLICATION EXERCISE 1.2

Subjective Type

1. A sample of clay was partially dried and then found to contain 50% silica and 7% water. The original clay contained 12% water. What is the percentage of silica in the original sample?
2. A 2.0 g of mixture of Na_2CO_3 and NaHCO_3 loses 0.248 g when heated to 300°C , the temperature at which NaHCO_3 decomposes to Na_2CO_3 , CO_2 , and H_2O . What is the percentage of Na_2CO_3 in mixture?
3. The molality of 1 M solution of sodium nitrate is $0.858 \text{ mol kg}^{-1}$. Determine the density of the solution. How much BaCl_2 would be needed to make 250 mL of a solution having same concentration of Cl^- as the one containing 3.78 g of NaCl per 100 mL?
4. 49 g of H_2SO_4 is dissolved in enough water to make one litre of a solution of density 1.049 g cc^{-1} . Find the molarity, normality, molality, and mole fraction of H_2SO_4 in the solution.
5. 4.0 g of a mixture of NaCl and Na_2CO_3 was dissolved in water and volume made up to 250 mL. 25 mL of this solution required 50 mL of N/10 HCl for complete neutralisation. Calculate the percentage composition of the original mixture.
6. 500 mL of 2M HCl , 100 mL of 2M H_2SO_4 , and one gram equivalent of a monoacidic alkali are mixed together. 30 mL of this solution required 20 mL of 143 g $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ in one litre solution. Calculate the water of crystallisation of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$.

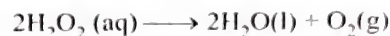
Objective Type

- i. A certain compound has the molecular formula X_4O_6 . If 10 g of X_4O_6 has 5.72 g X, then atomic mass of X is:
(1) 32 amu (2) 42 amu (3) 98 amu (4) 37 amu
- ii. For 109% labelled oleum, if the number of moles of

H_2SO_4 and free SO_3 be p and q , respectively, then what will be the value of $\frac{p-q}{p+q}$?

- (1) $1/9$ (2) 9 (3) 18 (4) $1/3$

- iii. Hydrogen peroxide in aqueous solution decomposes on warming to given oxygen according to the equation.



Under conditions where 1 mol of gas occupies 24 dm^3 , 100 cm^3 of $X \text{ M}$ solution of H_2O_2 produces 3 dm^3 of O_2 . Thus, X is

- (1) 2.5 (2) 0.5 (3) 0.25 (4) 1

- iv. 4 g of sulphur is burnt to form SO_2 , which is oxidised by Cl_2 water. The solution is then treated with BaCl_2 solution. The amount of BaSO_4 precipitated is:

- (1) 0.24 mol (2) 0.5 mol
(3) 1 mol (4) 0.125 mol

- v. A reaction occurs between 3 moles of H_2 and 1.5 moles of O_2 to give some amount of H_2O . The limiting reagent in this reaction is

- (1) H_2 and O_2 both (2) O_2
(3) H_2 (4) Neither of them

- vi. $4\text{I}^- + \text{Hg}^{2+} \longrightarrow \text{HgI}_4^{2-}$; 1 mole each of Hg^{2+} and I^- will form :

- (1) 1 mol of HgI_4^{2-}
(2) 0.5 mol of HgI_4^{2-}
(3) 0.25 mol of HgI_4^{2-}
(4) 2 mol of HgI_4^{2-}

8. i. The molarity of an aqueous solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 0.01. To 200 mL of the solution, which of the following should be carried out to make it 0.02 M?

I. Evaporate 50 mL of solution

II. Add 0.180 g of glucose and then evaporate 50 mL of solution

III. Add 50 mL of water

The correct option is:

- (1) I (2) III (3) II (4) I, II, III

- ii. The atomic mass of Cu is 63.546. There are only two naturally occurring isotopes of copper Cu^{63} and Cu^{65} . The percentage of natural abundance of Cu^{63} is nearly

- (1) 30 (2) 10 (3) 50 (4) 73

- iii. An aqueous solution of urea (NH_2CONH_2) is 3.0 molal. The mole fraction of urea is

- (1) 0.33 (2) 0.25 (3) 0.66 (4) 0.05

- iv. 0.2 M H_2SO_4 (1 mL) is diluted to 1000 times of its initial volume. The final normality of H_2SO_4 is:

- (1) 2×10^{-3} (2) 2×10^{-4} (3) 4×10^{-4} (4) 2×10^{-2}

- v. Which of the following quantities are dependent on temperature?

- (1) Molarity (2) Normality
(3) Mole fraction (4) Molality

vi. A sample of H_2SO_4 (density 1.8 g mL^{-1}) is 90% by weight. What is the volume of the acid that has to be used to make 1 L of 0.2 M H_2SO_4 ?
 (1) 16 mL (2) 18 mL (3) 12 mL (4) 10 mL

vii. The hydrated salt $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ undergoes 55.9% loss in weight on heating and becomes anhydrous. The value of n will be
 (1) 5 (2) 7 (3) 3 (4) 10

viii. 0.2 mol of HCl and 0.1 mol of barium chloride is dissolved in water to produce a 500 mL solution. The molarity of Cl^- is
 (1) 0.06 M (2) 0.12 M (3) 0.09 M (4) 0.80 M

ix. The density of 1 M solution of NaCl is 1.0585 g mL^{-1} . The molality of the solution is
 (1) 1.0585 (2) 1.00 (3) 0.0585 (4) 0.10

x. Hydrochloric acid solutions A and B have concentration of 0.5 N, and 0.1 N, respectively. The volume of solutions A and B required to make 2 L of 0.2 N hydrochloric acid are
 (1) 0.5 L of A + 1.5 L of B
 (2) 1.0 L of A + 1.0 L of B
 (3) 0.75 L of A + 1.25 L of B
 (4) 1.5 L of A + 0.5 L of B

9. i. H_3PO_4 is a tribasic acid and one of its salt is NaH_2PO_4 . What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4 ?
 (1) 100 mL (2) 200 mL
 (3) 80 mL (4) 300 mL

ii. Sulphuryl chloride, SO_2Cl_2 , reacts with H_2O to give mixture of H_2SO_4 and HCl. Aqueous solution of one mol SO_2Cl_2 will be neutralised by
 (1) 3 mol of NaOH (2) 2 mol of $\text{Ca}(\text{OH})_2$
 (3) Both (4) None

iii. The normality of a mixture obtained by mixing 100 mL of 0.2 M H_2SO_4 with 100 mL of 0.2 M NaOH is:
 (1) 0.05 N (2) 0.1 N (3) 0.15 N (4) 0.2 N

iv. 100 mL solution of 0.1 N HCl was titrated with 0.2 N NaOH solutions. The titration was discontinued after adding 30 mL of NaOH solution. The remaining titration was completed by adding 0.25 N KOH solution. The volume of KOH required from completing the titration is:
 (1) 70 mL (2) 35 mL (3) 32 mL (4) 16 mL

Fill in the Blanks Type

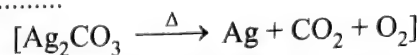
10. a. The equivalent weight of NaHCO_3 is and of SO_2 is

b. 2 mol of 50% pure $\text{Ca}(\text{HCO}_3)_2$ on heating forms 1 mol of CO_2 . The % yield of CO_2 is

c. 5 g of K_2SO_4 was dissolved in 250 mL of solution. The

volume of this solution that should be used so that 1.2 g of BaSO_4 may be precipitated from BaCl_2 is
 (molecular mass of $\text{K}_2\text{SO}_4 = 174$ and $\text{BaSO}_4 = 233$)

d. The residue obtained on strongly heating 2.76 g Ag_2CO_3 is



Atomic mass of Ag = 108

11. a. The mass of MgCl_2 should be dissolved in 750 g of water in order to prepare a 1.05 m solution is

b. The percentage composition (by mass) and mole fraction of each component in sugar solution containing 1000 g of sugar in 2000 g of water is

12. a. 2.24 L of ammonia at STP neutralised 100 mL of a solution of H_2SO_4 . The molarity of acid is

b. The equivalent weight of a metal carbonate 0.84 g of which reacts exactly with 40 mL of N/2 H_2SO_4 is

c. 1.575 g, of hydrated oxalic acid $(\text{COOH})_2 \cdot n\text{H}_2\text{O}$ is dissolved in water and the solution is made to 250 mL. On titration, 16.68 mL of this solution is required for neutralisation of 25 mL of N/15 NaOH. The value of water crystallisation, i.e., n , is

d. 1 mL of H_3PO_4 was diluted to 250 mL. 25 mL this solution required 40.0 mL of 0.10 N NaOH for neutralisation using phenolphthalein as indicator. The specific gravity of acid is

e. The density of 1.48 mass percent calcium hydroxide solution is 1.025 g mL^{-1} . The volume of 0.1 M HCl solutions required to neutralise 25 mL of this solution is

ANSWERS

Subjective Type

- 47.3%
- 66.4%
- $d = 1.25 \text{ g mL}^{-1}$, 16.8 g
- 0.5 M, 1.0 N, 0.5 m, 0.009
- 66.25%
- 10

Objective Type

- i. (1), ii. (1), iii. (1), iv. (4), v. (4), vi. (3)
- i. (3), ii. (4), iii. (4), iv. (3), v. (1), (2), vi. (3), vii. (4), viii. (4), ix. (2), x. (1)
- i. (2), ii. (2), iii. (2), iv. (4)

Fill in the Blanks Type

10. a. 88, 32, b. 100%, c. 44.8 mL, d. 2.16 g

11. a. 74.8 g, b. $\frac{200}{3}\%$, 0.97

12. a. 0.5 M, b. 42, c. 2, d. 1.32 g mL^{-1} , e. 102.54 mL

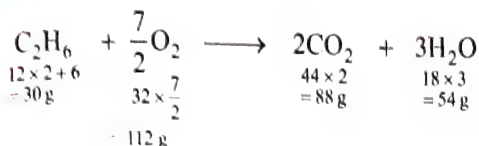
Solved Examples

Laws of Chemical Combination

EXAMPLE 1.1

3 g of ethane C_2H_6 on complete combustion gave 8.8 g of CO_2 and 5.4 g of water. Show that the results are in accordance with the law of conservation of mass.

Sol. First method:



a. 30 g of C_2H_6 = 88 g of CO_2

3 g of C_2H_6 = 8.8 g of CO_2

b. 30 g of C_2H_6 = 54 g of H_2O

3 g of C_2H_6 = 5.4 g of H_2O

c. 30 g of C_2H_6 = 112 g of O_2

3 g of C_2H_6 = 11.2 g of O_2

Weight of reactant = 3 + 11.2 = 14.2 g

Weight of product = 8.8 + 5.4 = 14.2 g

Hence, the law of conservation of mass is verified.

Second method:

Weights of C and H contained in 8.8 g of CO_2 and 5.4 g of H_2O are

$$\text{Weight of C in 8.8 g of } CO_2 = \frac{12 \times 8.8}{44} = 2.4 \text{ g}$$

$$\text{Weight of H in 5.4 g of } H_2O = \frac{2 \times 5.4}{18} = 0.6 \text{ g}$$

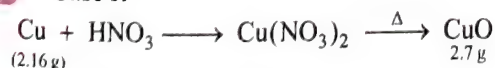
Total weight of C and H in the hydrocarbon after combustion = 2.4 + 0.6 = 3 g

Since the weight of C and H after combustion is the same as the weight of hydrocarbon before burning, the results are in accordance with the law of conservation of mass.

EXAMPLE 1.2

Weight of copper oxide obtained by heating 2.16 g of metallic copper with HNO_3 and subsequent ignition was 2.70 g. In another experiment, 1.15 g of copper oxide on reduction yielded 0.92 g of copper. Show that the results illustrate the law of definite proportions.

Sol. Case I:



Weight of oxygen = 2.7 - 2.16 = 0.54 g

$$\% \text{ of } O_2 \text{ in } CuO = \frac{0.54 \times 100}{2.7} = 20\%$$

Case II:

Copper oxide taken = 1.15 g

Copper left = 0.92 g

Oxygen present = 1.15 - 0.92 = 0.23 g

$$\% \text{ of } O_2 \text{ in } CuO = \frac{0.23 \times 100}{1.15} = 20\%$$

Percentage of oxygen is same in both the cases so law is verified. Similarly, the law can be verified by calculating the percent of Cu in both the cases.

EXAMPLE 1.3

In experiments on the effect of heating on oxides of lead in a current of hydrogen the following results were obtained. Show that they are in agreement with the law of multiple proportions.

- 1.393 g of litharge (PbO) gave 1.293 g of lead
- 2.173 g of lead peroxide (PbO_2) gave 1.882 g of lead
- 1.712 g of red lead (Pb_3O_4) gave 1.552 g of lead

Sol.

a. Weight of PbO = 1.393,

Weight of Pb = 1.293,

Weight of O_2 = 1.393 - 1.293 = 0.1 g

0.1 g of O_2 combines with 1.293 g of Pb.

1 g of O_2 combines with $\frac{1.293}{0.1} = 12.93$ g of Pb

b. Weight of PbO_2 = 2.173 g

Weight of Pb = 1.882 g

Weight of O_2 = 2.173 - 1.882 = 0.291 g

0.291 g of O_2 = 1.882 g of Pb

1 g of O_2 = $\frac{1.882}{0.291} = 6.46$ g. of Pb

c. Weight of Pb_3O_4 = 1.712 g

Weight of Pb = 1.552 g

Weight of O_2 = 1.712 - 1.552 = 0.16 g of O_2

\therefore 0.16 g of O_2 = 1.552 g of Pb

1 g of O_2 = $\frac{1.552}{0.16} = 9.7$ g. of Pb

Therefore, weight of Pb in three cases which combines with a fixed mass (1 g) of O_2

$$= 12.93 : 6.46 : 9.7$$

$$= \frac{12.93}{6.46} : \frac{6.46}{6.46} : \frac{9.7}{6.46} = 2 : 1 : 1.5$$

$$= 4 : 2 : 3$$

Hence, the law of multiple proportion is verified.

Alternatively, the weight of O_2 in three cases which combines with a fixed mass of Pb can also be calculated and they will also bear a simple whole number ratio, which proves the law of multiple proportions.

EXAMPLE 1.4

Two oxides of metal were found to contain 31.6% and 48% of oxygen, respectively. If the formula of first is represented by M_2O_3 , find that of the other.

Sol. First method:

First oxide	Second oxide
M_2O_3	M_2O_x
O = 31.6%	O = 48%
M = 68.4%	M = 52%

Let the atomic weight of the metal = M g
 $(2M + 48)$ g of M_2O_3 contains = $2M$ g of metal

$$100 \text{ g of } M_2O_3 \text{ contains} = \left(\frac{2M \times 100}{2M + 48} \right) = 68.4$$

Solve for $M = 52$

Atomic weight of metal = 52

Therefore, in second oxide:

$$O = \frac{48}{16} = 3 \quad M = \frac{52}{52} = 1$$

Therefore, formula = MO_3

Second method:

First oxide:

68.4 g of M contains = 31.6 g of oxygen

$$52 \text{ g of } M \text{ contains} = \frac{31.6 \times 52}{68.4} = 24 \text{ g of } O_2$$

Ratio of O in M_2O_3 and M_2O_x = $24:48$ (given) = $1:2$

Therefore, the ratio of O in second oxide should be twice the oxygen in first oxide and the % of M is fixed.

Therefore, first oxide = M_2O_3

Second oxide = M_2O_6 or MO_3

Third method:

a. 68.4 g of M in first oxide = 2 atoms of M

$$52 \text{ g of } M \text{ contains} = \frac{2 \times 52}{68.4} = 1.5 \text{ atoms of } M$$

b. 31.6 g of oxygen in first oxide contains = 3 atoms of oxygen

$$48 \text{ g of oxygen contains} = \frac{3 \times 48}{31.6} = 4.5 \text{ atoms of oxygen}$$

$$\text{Ratio of } M:O = 1.5 : 4.5 = 1 : 3$$

Thus, the formula is MO_3 .

EXAMPLE 1.5

A, B, and C are three elements giving compounds AB, AC, and BC. AB contains 75% of A, AC contains 57.14% of C, and BC contains 11.11% of B. Show that the results illustrate the law of reciprocal proportions.

Sol. AB = 75% A, 25% B

AC = 42.86% A, 57.14% C

BC = 11.11% B, 88.89% C

In AB:

25 g of B combines with 75 g of A.

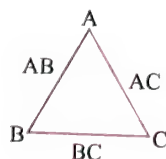
$$1 \text{ g of B combines with } \frac{75}{25} = 3 \text{ g of A.}$$

In BC:

11.11 g of B combines with 88.89 g of C.

$$1 \text{ g of B combines with } \frac{88.89}{11.11} = 8 \text{ g of C.}$$

Ratio of A and C which combines with a fixed mass of B
 $(1 \text{ g}) = 3 : 8.$



Similarly, the ratio of A and C in AC = $42.86 : 57.14$

$$= \frac{42.86}{42.86} : \frac{57.14}{42.86} = 1 : 1.333$$

The two ratios are $A:C$

$$\frac{3}{1} : \frac{8}{1.333}$$

$$3 : 6$$

$$1 : 2$$

Hence, the law of reciprocal proportions is verified.

EXAMPLE 1.6

A metal forms two oxides. The higher oxide contains 80% metal. 0.72 g of the lower oxide gave 0.8 g of higher oxide when oxidised. Calculate the weight of oxygen that combines with the fixed weight of the metal in the two oxides, and show that the data supports the law of multiple proportions.

Sol. First method:

Since, 0.8 g of higher oxide is obtained from 0.72 g of lower oxide, therefore, the weight of lower oxide that would produce 100 g of higher oxide on oxidation

$$= \frac{0.72 \times 100}{0.80} = 90 \text{ g}$$

Thus, 90 g of lower oxide contains as much metal as 100 g of higher oxide, i.e., 80 g (given).

Hence, 80 g of metal combines with 10 g of oxygen in the lower oxide and 20 g of oxygen in the higher oxide. The weights of oxygen that combine with the same weight of the metal in the two oxides are in the ratio of 10:20 or 1:2. The ratio, being simple, proves the law of multiple proportions.

Second method: Lower oxide + $O_2 \rightarrow$ Higher oxide

Lower oxide: 0.72 g

Weight of oxide = 0.72 g

Weight of M (fixed weight) = 0.64 g

Weight of O_2 = $0.72 - 0.64 = 0.08$ g of O_2

Higher oxide: 0.2 g

100 g of oxide contains \Rightarrow 80 g of M

$$0.8 \text{ g of oxide contains} \Rightarrow \frac{80}{100} \times 0.8 \Rightarrow 0.64 \text{ g of } M$$

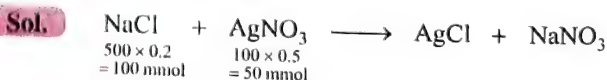
Weight of O_2 = $0.8 - 0.64 = 0.16$ g of O_2

Ratio of oxygen in lower oxide and higher oxide
 $= 0.08 : 0.16 \Rightarrow 1:2$

Limiting Reagent

EXAMPLE 1.7

500 mL of 0.2 M NaCl sol. is added to 100 mL of 0.5 M $AgNO_3$ solution resulting in the formation of white precipitate of $AgCl$. How many moles and how many grams of $AgCl$ are formed? Which is the limiting reagent?



50 mmol of AgNO_3 will react with 50 mmol of NaCl and 50 mmol of AgCl will be formed.

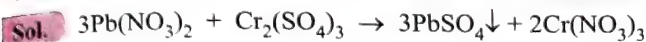
$$\text{AgCl} = 50 \text{ mmol} = 50 \times 10^{-3} = 0.05 \text{ mol}$$

$$\text{Weight of AgCl} = 0.05 \times 143.5 = 7.175 \text{ g}$$

Hence, AgNO_3 is the limiting reagent.

EXAMPLE 1.8

Upon mixing 50.0 mL of 0.1 M lead nitrate solution with 50.0 mL of 0.05 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also, calculate the molar concentration of the species left behind in the final solution. Which is the limiting reagent?



	3 mmol	1 mmol	3 mmol	2 mmol
Initial	50×0.1	50×0.05		
	= 5 mmol	2.5 mmol		

a. $3 \text{ mmol of Pb}(\text{NO}_3)_2 = 1 \text{ mmol of Cr}(\text{SO}_4)_3$

$$5 \text{ mmol of Pb}(\text{NO}_3)_2 = \frac{1}{3} \times 5 = 1.66 \text{ mmol}$$

b. Since $\text{Pb}(\text{NO}_3)_2$ is completely consumed, so it is a limiting reagent.

$$\text{Cr}_2(\text{SO}_4)_3 \text{ left} = 2.5 - 1.66 = 0.833 \text{ mmol}$$

$$3 \text{ mmol of Pb}(\text{NO}_3)_2 = 3 \text{ mmol of PbSO}_4$$

$$\begin{aligned} 5 \text{ mmol of Pb}(\text{NO}_3)_2 &= 5 \text{ mmol of PbSO}_4 \\ &= 5 \times 10^{-3} \text{ mol} \\ &= 0.005 \text{ mol of PbSO}_4 \end{aligned}$$

c. $3 \text{ mmol of Pb}(\text{NO}_3)_2 = 2 \text{ mmol of Cr}(\text{NO}_3)_3$

$$5 \text{ mmol of Pb}(\text{NO}_3)_2 = \frac{2}{3} \times 5 = 3.33 \text{ mmol}$$

$$\text{Total volume} = 50 + 50 = 100 \text{ mL}$$

$$\text{Concentration of Cr}(\text{NO}_3)_3 \text{ in the solution}$$

$$= \frac{\text{mmol}}{\text{mL}} = \frac{3.33}{100} = 0.033 \text{ M}$$

d. Concentration of $\text{Cr}_2(\text{SO}_4)_3$ left = $\frac{0.833}{100} = 0.0083 \text{ M}$

Empirical and Molecular Formulae

EXAMPLE 1.9

What is the percentage of aluminium in Al_2O_3 ? ($\text{Al} = 27$, $\text{O} = 16$).

Sol. $M_w \text{ of Al}_2\text{O}_3 = 27 \times 2 + 16 \times 3 = 102 \text{ g}$

$$\% \text{ of Al} = \frac{54 \times 100}{102} = 52.94\%$$

EXAMPLE 1.10

What is the percentage composition of each element in zinc-phosphate $\text{Zn}_3(\text{PO}_4)_2$? ($\text{Zn} = 65.5$, $\text{P} = 31$, $\text{O} = 16$)

Sol. $M_w \text{ of Zn}_3(\text{PO}_4)_2 = 65.5 \times 3 + 2[31 + 16 \times 4]$
 $= 196.5 + 2 \times 95 = 386.5$

$$\% \text{ of Zn} = \frac{196.5 \times 100}{386.5} = 50.84\%$$

$$\% \text{ of P} = \frac{62 \times 100}{386.5} = 16.04\%$$

$$\% \text{ of O} = \frac{128 \times 100}{386.5} = 33.12\%$$

EXAMPLE 1.11

An organic compound consists of 6.023×10^{23} carbon atoms, 1.8069×10^{24} hydrogen atoms, and 3.0115×10^{23} oxygen atoms. What is its simplest formula?

Sol. Moles of C = $\frac{6.023 \times 10^{23}}{6.023 \times 10^{23}} = 1$

$$\text{Moles of H} = \frac{1.8069 \times 10^{24}}{6.023 \times 10^{23}} = 3$$

$$\text{Moles of O} = \frac{3.0115 \times 10^{23}}{6.023 \times 10^{23}} = 0.5$$

$$\text{C : H : O} = 1 : 3 : 0.5 = 2 : 6 : 1$$

$$\text{Empirical formula} = \text{C}_2\text{H}_6\text{O}$$

EXAMPLE 1.12

What is the simplest formula of a compound that contains 0.25 g atom of silicon per 0.50 g atom of oxygen?

Sol. 0.25 g atom or mol of Si = 0.5 mol of oxygen

$$1 \text{ mol of Si} = \frac{0.5}{0.25} = 2 \text{ mol of oxygen}$$

$$\text{Formula: SiO}_2$$

EXAMPLE 1.13

0.1653 g aluminium reacts completely with 0.652 g chlorine to form chloride of aluminium.

a. What is the empirical formula of the compound?

b. If molecular mass of the compound is 267 amu, calculate the molecular formula of the compound.

Sol. 0.1653 g of Al = 0.652 g of chlorine

a. $27 \text{ g of Al} = \frac{0.652}{0.1653} \times 27$
 $= 106.95 \text{ g of chlorine}$

$$\text{Moles of Chlorine} = \frac{106}{35.5} = 2.998 \approx 3$$

$$\text{Therefore, formula} = \text{AlCl}_3$$

b. $M_w = 267 \text{ g}$

$$\begin{aligned} \text{Empirical formula weight of AlCl}_3 &= 27 + 3 \times 35.5 \\ &= 133.5 \end{aligned}$$

$$n = \frac{M_w}{E.F.w} = \frac{267}{133.5} = 2$$

$$\text{Molecular formula} = 2 \times \text{AlCl}_3 = \text{Al}_2\text{Cl}_6$$

EXAMPLE 1.14

A 0.2075 g sample of an oxide of cobalt on analysis was found to contain 0.1475 g cobalt. Calculate the empirical formula of the oxide. (Co = 59 amu)

Sol. Weight of O = 0.2075 - 0.1475 = 0.06 g

$$\text{Mol of Co} = \frac{0.1475}{59} = 0.0025$$

$$\text{Mol of O} = \frac{0.06}{16} = 0.003$$

$$\text{Simplest ratio of Co} = \frac{0.0025}{0.0025} = 1.0$$

$$\text{Simplest ratio of O} = \frac{0.003}{0.0025} = 1.5$$

$$\text{Ratio of Co : O} = 1 : 1.5 = 2 : 3.$$

$$\text{Formula} = \text{Co}_2\text{O}_3$$

EXAMPLE 1.15

The molecular mass of an iodide of tin (Sn) is 626.5 amu. What is the empirical formula of the substance? (I = 127, Sn = 118.5)

Sol. Let the formula of iodide of Sn = SnI_x

Since the valency of Iodide = -1

$$\therefore \text{SnI}_x = 118.5 + 127 \times x = 625.5$$

Solve for x:

$$\therefore x = 4$$

$$\text{Formula} = \text{SnI}_4$$

EXAMPLE 1.16

✓ What is the empirical formula for a compound that contains 22% S and 78% F? (S = 32, F = 19)

Sol.

Element	Moles	Least ratio
S	$\frac{22}{32} = 0.6875$	$\frac{0.6875}{0.6875} = 1$
F	$\frac{78}{19} = 4.10$	$\frac{4.10}{0.6875} = 5.97 \approx 6$

$$\text{Formula} = \text{SF}_6$$

EXAMPLE 1.17

A substance used as a water softener has the following mass percentage composition : 42.07% Na, 18.9% P, and 39.04% of oxygen. Determine the empirical formula of the compound. (Na = 23, P = 31, O = 16)

Sol.

Element	Moles	Least ratio
Na	$\frac{42.07}{23} = 1.829$	$\frac{1.829}{0.6} = 3$
P	$\frac{18.9}{31} = 0.6$	$\frac{0.6}{0.6} = 1$

$$\text{O} \quad \frac{39.04}{16} = 2.44 \quad \frac{2.44}{0.6} = 4$$

$$\text{Empirical formula} = \text{Na}_3\text{PO}_4$$

EXAMPLE 1.18

An organic compound contains 43.98% C, 2.09 % H, and 37.2% Cl. Calculate its empirical formula.

Sol. Oxygen = 100 - 43.98 - 2.09 - 37.2 = 16.73.

Element	Moles	Least ratio	Whole number ratio
C	$\frac{43.98}{12} = 3.66$	$\frac{3.66}{1.04} = 3.5$	7
H	$\frac{2.09}{1} = 2.09$	$\frac{2.09}{1.04} = 2$	4
Cl	$\frac{37.2}{35.5} = 1.04$	$\frac{1.04}{1.04} = 1$	2
O	$\frac{16.73}{16} = 1.04$	$\frac{1.04}{1.04} = 1$	2

$$\text{Empirical formula} = \text{C}_7\text{H}_4\text{Cl}_2\text{O}_2$$

EXAMPLE 1.19

A 0.534 g of a sample of haemoglobin on analysis was found to contain 0.34% Fe. If each haemoglobin molecule has four Fe^{2+} ions, what is the molecular mass of haemoglobin? (Fe = 56 amu)

Sol. 100 g of haemoglobin contains = 0.34 g of Fe

1 mol of haemoglobin contains = 4Fe^{2+} ions

$$= 4 \times 56 \text{ g} = 224 \text{ g}$$

\therefore 0.34 g of Fe is present in 100 g of haemoglobin

$$224 \text{ g of Fe is present in} = \frac{100 \times 224}{0.34} = 65882.4 \text{ g}$$

$$M_w \text{ of haemoglobin} = 65882.4 \text{ g}$$

Avogadro's Hypothesis and Mole Concept**EXAMPLE 1.20**

How many g atoms and number of atoms are there in (a) 60 g carbon, (b) 224.4 g Cu, and (c) 72.52 g lead. Given atomic masses of C, Cu, and Pb are 12, 63.6, and 207.2, respectively. (Avogadro's number = 6.02×10^{23}).

Sol. $\text{g atom} = \frac{\text{Weight}}{\text{Atomic weight}}$

$$\text{and number of atoms} = \frac{\text{Weight} \times N_A}{\text{Atomic weight}}$$

a. For 60 g C:

$$\text{g atom} = \frac{60}{12} = 5$$

$$\text{Number of atoms} = \frac{224.4 \times 6.02 \times 10^{23}}{63.6} = 30.1 \times 10^{23}$$

b. For 224.4 g Cu:

$$\text{g atom} = \frac{224.4}{63.6} = 3.53$$

$$\text{Number of atoms} = \frac{224.4 \times 6.02 \times 10^{23}}{63.6} = 21.24 \times 10^{23}$$

c. For 72.52 g Pb:

$$\text{g atom} = \frac{72.52}{207.2} = 0.35$$

$$\text{Number of atoms} = \frac{72.52 \times 6.02 \times 10^{23}}{207.2} = 2.107 \times 10^{23}$$

EXAMPLE 1.21

Find the number of g atoms and weight of an element having 2×10^{23} atoms. Atomic mass of element is 32.

Sol. N atoms have 1 g atom

$$\therefore 2 \times 10^{23} \text{ atoms} = \frac{2 \times 10^{23}}{6.023 \times 10^{23}} = 0.33 \text{ g atom}$$

$\therefore N$ atoms of element weight 32 g

$\therefore 2 \times 10^{23}$ atoms of element weigh

$$= \frac{32 \times 2 \times 10^{23}}{6.023 \times 10^{23}} = 10.63 \text{ g}$$

EXAMPLE 1.22

Calculate the number of atoms and volume of 1 g helium gas at STP.

Sol. 4 g helium has 6.023×10^{23} atoms

$$\therefore 1 \text{ g helium has } \frac{6.023 \times 10^{23}}{4} \text{ atoms}$$

$$= 1.506 \times 10^{23} \text{ atoms}$$

Also,

$\therefore 4 \text{ g helium has volume at STP} = 22.4 \text{ L}$

$$\therefore 1 \text{ g helium has volume at STP} = \frac{22.4}{4} = 5.6 \text{ L}$$

EXAMPLE 1.23

From 200 mg of CO_2 , 10^{21} molecules are removed. How many grams and moles of CO_2 are left?

Sol. 6.023×10^{23} molecules of $\text{CO}_2 = 44 \text{ g}$

$$\therefore 10^{21} \text{ molecules of } \text{CO}_2 = \frac{44 \times 10^{21}}{6.023 \times 10^{23}}$$

$$= 7.31 \times 10^{-2} = 73.1 \text{ mg}$$

$$\therefore \text{CO}_2 \text{ left} = 200 - 73.1 = 126.9 \text{ mg}$$

$$\text{Also, moles of } \text{CO}_2 = \frac{\text{Weight}}{\text{Molecular weight}} = \frac{126.9 \times 10^{-3}}{44} = 2.88 \times 10^{-3}$$

EXAMPLE 1.24

Weight of one atom of an element is $6.644 \times 10^{-23} \text{ g}$. Calculate g atom of element in 40 kg.

Sol. Weight of 1 atom of element = $6.644 \times 10^{-23} \text{ g}$

Weight of N atom of element

$$= 6.644 \times 10^{-23} \times 6.023 \times 10^{23}$$

$$= 40$$

$\therefore 40 \text{ g weight of element has } 1 \text{ g atom.}$

$\therefore 40 \times 10^{-23} \text{ g weight of element}$

$$= \frac{40 \times 10^{-23}}{40} = 10^{-23} \text{ g atom}$$

EXAMPLE 1.25

How many g of S are required to produce 100 mol and 100 g H_2SO_4 separately?

Sol. 1 mol of H_2SO_4 has = 32 g S

$$\therefore 100 \text{ mol of } \text{H}_2\text{SO}_4 \text{ has} = 32 \times 100 = 3200 \text{ g S}$$

$$\therefore 98 \text{ g } \text{H}_2\text{SO}_4 \text{ has S} = 32 \text{ g}$$

$$\therefore 100 \text{ g } \text{H}_2\text{SO}_4 \text{ has S} = \frac{32 \times 100}{98} = 32.65 \text{ g S}$$

EXAMPLE 1.26

Calculate the number of oxalic acid molecules in 100 mL of 0.02 N oxalic acid.

Sol. Normality = 0.02

$$\therefore \text{Molarity} = \frac{0.02}{2} \quad (\because \text{Valency factor} = 2)$$

$$\therefore \text{Moles of oxalic acid} = \frac{0.02}{2} \times \frac{100}{1000}$$

$$(\because \text{Moles} = M \times V_L)$$

\therefore Number of molecules of oxalic acid

$$= 0.001 \times 6.023 \times 10^{23}$$

$$= 6.023 \times 10^{20}$$

EXAMPLE 1.27

Haemoglobin contains 0.25% iron by weight. The molecular weight of haemoglobin is 89600. Calculate the number of iron atom per molecule of haemoglobin.

Sol. 100 g haemoglobin has = 0.25 g Fe

$$\therefore 89600 \text{ g haemoglobin has} = \frac{0.25 \times 89600}{100}$$

$$= 224 \text{ g Fe}$$

\therefore 1 mol or N molecules of haemoglobin has

$$= \frac{224}{56} \text{ g atom Fe}$$

$$4 \text{ g atom Fe}$$

Therefore, 1 molecule of haemoglobin has 4 atoms of Fe.

EXAMPLE 1.28

P and Q are two elements that form P_2Q_3 and PQ_2 . If 0.15 mole of P_2Q_3 weighs 15.9 g and 0.15 mole of PQ_2 weighs 9.3 g, what are the atomic weights of P and Q?

Sol. Let the atomic weights of P and Q are a and b , respectively.

$$\therefore \text{Molecular weight of } P_2Q_3 = 2a + 3b$$

$$\text{and molecular weights of } PQ_2 = a + 2b$$

Now given that 0.15 mole of P_2Q_3 weighs 15.9 g

$$(2a + 3b) = \frac{15.9}{0.15} \quad \left(\because \frac{\text{Weight}}{\text{Molecular weight}} = \text{mole} \right)$$

$$\text{Similarly, } a + 2b = \frac{9.3}{0.15}$$

Solving these two equations

$$b = 18$$

$$a = 26$$

Mole Concept in Solution

EXAMPLE 1.29

Find the milli equivalent of

a. Ca(OH)_2 in 74 g b. NaOH in 20 g

c. H_2SO_4 in 2.45 g

Sol. $\text{mEq of Ca(OH)}_2 = \frac{W}{E} \times 1000 = \frac{74}{74/2} \times 1000 = 2000$

$$\begin{aligned} \text{mEq of NaOH} &= \frac{20}{40} \times 1000 & (\because E_{\text{NaOH}} = 40) \\ &= 500 \end{aligned}$$

$$\begin{aligned} \text{mEq} &= \frac{2.45}{49} \times 1000 & (\because E_{\text{H}_2\text{SO}_4} = 49) \\ &= 50 \end{aligned}$$

EXAMPLE 1.30

Calculate the normality of NaOH when 2 g is present in 800 mL solution.

Sol. $N = \frac{\text{Equivalent}}{V_{\text{sol}} (\text{in L})}$

$$\therefore \text{Equivalent of NaOH} = \frac{2}{40}$$

$$\text{and volume of solution} = \frac{800}{1000} \text{ L}$$

$$\therefore N = \frac{2 \times 1000}{40 \times 800} = 0.0625$$

EXAMPLE 1.31

Calculate normality and molarity of the following:

a. 0.74 g of Ca(OH)_2 in 5 mL of solution.

b. 3.65 g of HCl in 200 mL of solution.

c. 1/10 mol of H_2SO_4 in 500 mL of solution.

Sol.

a. $\therefore \text{Equivalent of Ca(OH)}_2 = \frac{0.74}{74/2} \left(\text{Eq} = \frac{W_2}{E_{w_2}} \right)$

$$\text{Volume of solution} = 5 \text{ mL}$$

$$\therefore N = \frac{0.74 \times 1000 \times 2}{74 \times 5} = 4$$

$$\therefore M = \frac{N}{\text{Valency}} = \frac{4}{2} = 2$$

b. $\therefore \text{Equivalent of HCl} = \frac{3.65}{36.5}$

$$\text{and Volume of solution} = 200 \text{ mL}$$

$$\therefore N = \frac{3.65 \times 1000}{36.5 \times 200} = 0.5$$

$$\text{and } M = \frac{N}{\text{Valency}} = \frac{0.5}{1} = 0.5$$

c. $\text{Equivalent of H}_2\text{SO}_4 = \frac{1}{10} \times 2$

$$(\because \text{Eq} = \text{Mole} \times \text{Valency})$$

$$\text{Volume of solution} = 500 \text{ mL}$$

$$\therefore N = \frac{2 \times 1000}{10 \times 500} = 0.4$$

$$M = \frac{0.4}{2} = 0.2$$

EXAMPLE 1.32

Calculate the normality of the resulting solution made by adding 2 drops (0.1 mL) of 0.1N H_2SO_4 in 1 litre of distilled water.

Sol. mEq of solute does not change on dilution

$$\therefore \text{mEq of H}_2\text{SO}_4 (\text{conc}) = \text{mEq of H}_2\text{SO}_4 (\text{dil})$$

$$0.1 \times 0.1 = N \times 1000 \quad (\because \text{mEq} = N \times V_{\text{sol}} \text{ in mL})$$

$$N = 10^{-5}$$

EXAMPLE 1.33

What volume at STP of ammonia gas will be required to be passed into 30 mL of N H_2SO_4 solution to bring down the acid normality to 0.2 N?

Sol. $\text{mEq of original H}_2\text{SO}_4 = 30 \times 1 = 30$

$$\text{mEq of H}_2\text{SO}_4 \text{ after passing NH}_3 = 30 \times 0.2 = 6$$

$$\therefore \text{mEq of H}_2\text{SO}_4 \text{ lost} = 30 - 6 = 24$$

$$\therefore \text{mEq of NH}_3 \text{ passed} = \text{mEq of H}_2\text{SO}_4 \text{ lost}$$

$$\therefore \frac{W}{17} \times 1000 = 24$$

$$\therefore W_{\text{NH}_3} = 0.408 \text{ g}$$

$$\therefore \text{Volume of NH}_3 \text{ of STP} = \frac{22.4 \times 0.408}{17}$$

$$= 0.5376 \text{ L} = 537.6 \text{ mL}$$

EXAMPLE 1.34

Calculate the normality of mixture obtained by mixing

- 100 mL of 0.1 N HCl + 50 mL of 0.25 N NaOH
- 100 mL of 0.2 M H₂SO₄ + 200 mL of 0.2 M HCl
- 100 mL of 0.2 M H₂SO₄ + 100 mL of 0.2 M NaOH
- 1 g equivalent of NaOH + 100 mL of 0.1 N HCl

Sol.

a. mEq of HCl = $100 \times 0.1 = 10$

mEq of NaOH = $50 \times 0.25 = 12.5$

Because HCl and NaOH neutralise each other with equal equivalents

mEq of NaOH left = $12.5 - 10 = 2.5$

Volume of new solution = $100 + 50 = 150$ mL

$\therefore N_{\text{NaOH}} \text{ left} = \frac{2.5}{150} = 0.0167$

b. mEq of H₂SO₄ = $100 \times 0.2 \times 2$ ($\because N = M \times \text{Valency}$)
= 40

mEq of HCl = $200 \times 0.2 \times 1 = 40$

\therefore Total mEq of acid = $40 + 40 = 80$

Total volume of solution = 300 mL

$\therefore N_{\text{Acid solution}} = \frac{80}{300} = 0.267$

c. mEq of H₂SO₄ = $100 \times 0.2 \times 2 = 40$

mEq of NaOH = $100 \times 0.2 \times 1 = 20$

\therefore mEq of H₂SO₄ left after reaction = $40 - 20 = 20$

Total volume of solution = $100 + 100 = 200$ mL

$\therefore N_{\text{H}_2\text{SO}_4} \text{ left} = \frac{20}{200} = 0.1$

d. mEq of NaOH = $1 \times 1000 = 1000$

mEq of HCl = $100 \times 0.1 = 10$

\therefore mEq of NaOH left after reaction = $1000 - 10 = 990$

Total volume of solution = 100 mL

$\therefore N_{\text{NaOH}} \text{ left} = \frac{990}{100} = 9.9$

EXAMPLE 1.35

In what ratio should you mix 0.2 M NaNO₃ and 0.1 M Ca(NO₃)₂ solution so that in resulting solution, the concentration of -ve ions is 50% greater than the concentration of +ve ions?

Sol. Let V_1 mL of NaNO₃ is mixed with V_2 mL of Ca(NO₃)₂.

mmoles of NaNO₃ mixed = $0.2 \times V_1$

mmoles of Ca(NO₃)₂ mixed = $0.1 \times V_2$

\therefore Mol ratio of Ca²⁺: NO₃⁻ in Ca(NO₃)₂ is 1:2.

\therefore Molarity of NO₃⁻ in the mixture

$$= [\text{NO}_3^-] \text{ of NaNO}_3 + [\text{NO}_3^-] \text{ of Ca(NO}_3)_2$$

$$= \frac{0.2 \times V_1}{(V_1 + V_2)} + \frac{0.1 \times 2 \times V_2}{(V_1 + V_2)}$$

$$= \frac{0.2V_1 + 0.2V_2}{V_1 + V_2}$$

Similarly, molarity of Na⁺ and Ca²⁺ in mixture

$$= \frac{0.2 \times V_1}{V_1 + V_2} + \frac{0.1 \times V_2}{V_1 + V_2}$$

$$= \frac{0.2V_1 + 0.1V_2}{V_1 + V_2}$$

Now given that

$$\text{Molarity of NO}_3^- = \frac{3}{2} \text{ Molarity of Na}^+ \text{ and Ca}^{2+}$$

$$\therefore \frac{0.2V_1 + 0.2V_2}{V_1 + V_2} = \frac{3}{2} \left(\frac{0.2V_1 + 0.1V_2}{V_1 + V_2} \right)$$

$$\therefore \frac{V_1}{V_2} = \frac{1}{2}$$

EXAMPLE 1.36

What volume of water is required to make 0.20 N solution from 1600 mL of 0.2050 N solution?

Sol. mEq of concentrated solution = $1600 \times 0.2050 = 328$

Let after dilution volume becomes V mL.

mEq of diluted solution = $0.20 \times V$

$\therefore 328 = 0.20 \times V$

$V = 1640$ mL

Thus, the volume of water used to prepare 1640 mL of 0.20 N solution = $1640 - 1600 = 40$ mL

EXAMPLE 1.37

20 mL of 0.2 M Al₂(SO₄)₃ is mixed with 20 mL of 0.6 M BaCl₂. Calculate the concentration of each ion in solution.

Sol.

	Al ₂ (SO ₄) ₃	+	BaCl ₂	→	BaSO ₄ ↓	+ AlCl ₃
mEq before	$20 \times 0.2 \times 6$		$20 \times 0.6 \times 2$		0	0
mixing	= 24		= 24			
mEq after	0		0		24	24

mixing

mEq = $N \times V$ (in mL) = $M \times \text{Valency}$

$\therefore [\text{Al}^{3+}] = \frac{24}{40 \times 3} = 0.2$ M

Total volume = $20 + 20 = 40$ mL

$[\text{Cl}^-] = \frac{24}{40} = 0.6$ M

No concentration of Ba²⁺ or SO₄²⁻ in the solution since BaSO₄ gets precipitated.

EXAMPLE 1.38

How much BaCl_2 would be needed to make 250 mL of a solution having same concentration of Cl^- as the one containing 3.78 g of NaCl per 100 mL.

$$\text{Sol. } N_{\text{NaCl}} = \frac{3.78 \times 1000}{58.5 \times 100} = 0.646$$

Let W g of BaCl_2 is dissolved in 250 mL, then

$$N_{\text{BaCl}_2} = \frac{W}{\frac{208}{2} \times \frac{250}{1000}} = 0.0385W$$

$\therefore [\text{Cl}^-]$ in both is same

$$\therefore N_{\text{NaCl}} = N_{\text{BaCl}_2}$$

$$\therefore 0.646 = 0.0385W$$

$$\therefore W = 16.80 \text{ g}$$

PERCENTAGE V/V**EXAMPLE 1.39**

Calculate the molarity and molality of 20% aqueous ethanol ($\text{C}_2\text{H}_5\text{OH}$) solution by volume. (density of solution = 0.96 g mL^{-1})

Sol. $\text{C}_2\text{H}_5\text{OH}$ is 20% by volume, i.e., 20 mL of $\text{C}_2\text{H}_5\text{OH}$ is dissolved in 100 mL of solution.

$$\text{Volume of } \text{H}_2\text{O} = 100 - 20 = 80 \text{ mL}$$

$$\text{Weight of } \text{H}_2\text{O} = 80 \times 1 = 80 \text{ g } (d_{\text{H}_2\text{O}} = 1)$$

$$\text{Weight of solution} = 100 \times 0.96 = 96 \text{ g}$$

$$\text{Weight of } \text{C}_2\text{H}_5\text{OH} = 96 - 80 = 16 \text{ g}$$

$$(M_w \text{ of } \text{C}_2\text{H}_5\text{OH} = 12 \times 2 + 5 + 16 + 1 = 46)$$

$$\therefore M = \frac{W_2 \times 1000}{Mw_2 \times V_{\text{sol}}} = \frac{16 \times 1000}{46 \times 100} = 3.48$$

$$m = \frac{W_2 \times 1000}{Mw_2 \times W_1} = \frac{16 \times 1000}{46 \times 80} = 4.35$$

EXAMPLE 1.40

If 4 g NaOH are dissolved in 100 mL of aqueous solution, what will be the difference in its normality and molarity?

Sol. (M_w of $\text{NaOH} = 23 + 16 + 1 = 40$)

$$M = \frac{W_2 \times 1000}{Mw_2 \times V_{\text{sol}}} = \frac{4 \times 1000}{40 \times 100} = 1$$

(Since NaOH is monobasic acid its normality and molarity will be same)

EXAMPLE 1.41

An aqueous solution of dibasic acid (molecular mass = 118) containing 35.4 g of acid per litre of the solution has density 1.0077 g mL^{-1} .

Express the concentration in as many ways as you can?

$$\text{Sol. } M = \frac{35.4 \times 1000}{118 \times 1000} = 0.3$$

$$m = \frac{W_2 \times 1000}{Mw_2 \times (V_{\text{sol}} \times d_{\text{sol}} - W_2)} = \frac{35.4 \times 1000}{118 (1000 \times 1.0077 - 35.4)}$$

$$= \frac{35.4 \times 1000}{118 \times 972.3} = 0.31$$

$$N = n \times M = 2 \times 0.3 = 0.6$$

Weight of solvent (W_1)

$$= \text{Weight of solution} - \text{Weight of solute}$$

$$= V_{\text{sol}} \times d_{\text{sol}} - W_2$$

$$= 1000 \times 1.0077 - 35.4 = 972.3$$

$$\begin{aligned} \chi_2 &= \frac{n_2}{n_1 + n_2} = \frac{W_2 / M_{w_2}}{\frac{W_1}{M_{w_1}} + \frac{W_2}{M_{w_2}}} \\ &= \frac{35.4 / 118}{\frac{972.3}{18} + \frac{35.4}{118}} \\ &= \frac{0.3}{54 + 0.3} = 0.0055 \end{aligned}$$

$$\chi_1 = 1 - \chi_2 = 1 - 0.0055 = 0.9945$$

EXAMPLE 1.42

A solution contains 2.80 moles of acetone (CH_3COCH_3) and 8.20 mole of CHCl_3 . Calculate the mole fraction of acetone.

$$\text{Sol. } \chi_2 = \frac{n_2}{n_1 + n_2} = \frac{2.80}{8.2 + 2.8} = \frac{2.8}{11} = 0.255$$

EXAMPLE 1.43

The percentage composition (by weight) of a solution is 45% X, 15% Y, and 40% Z. Calculate the mole fraction of each component of the solution. (Molecular mass of X = 18, Y = 60, and Z = 60)

$$\text{Sol. } X = 45\%, n_1 = \frac{45}{18} = 2.5$$

$$Y = 15\%, n_2 = \frac{15}{60} = 0.25$$

$$Z = 40\%, n_3 = \frac{40}{60} = 0.666$$

$$\begin{aligned} \chi_1 &= \frac{n_1}{n_1 + n_2 + n_3} = \frac{2.5}{2.5 + 0.25 + 0.666} \\ &= \frac{2.5}{3.416} = 0.73 \end{aligned}$$

$$x_2 = \frac{n_2}{n_1 + n_2 + n_3} = \frac{0.25}{3.416} = 0.073$$

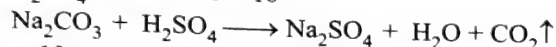
$$x_3 = [1 - (x_1 + x_2)] = (1 - 0.73 - 0.073) = 0.195$$

EXAMPLE 1.44

What is the normality and nature of a mixture obtained by mixing 0.62 g of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ to 100 mL of 0.1 N H_2SO_4 ?

Sol. mEq of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = \frac{0.62}{62} \times 1000 \left(\frac{W}{E} \times 1000 = \text{mEq} \right)$
 $= 10$

$$\text{mEq of } \text{H}_2\text{SO}_4 = 100 \times 0.1 = 10$$



$$\begin{array}{ccccc} \text{mEq added} & 10 & 10 & 0 & 0 & 0 \\ \text{mEq left} & 0 & 0 & 10 & 10 & 10 \end{array}$$

$$\therefore N_{\text{Na}_2\text{SO}_4} = \frac{10}{100} = 0.1$$

Solution becomes neutral since both acid and base are used up and Na_2SO_4 does not show hydrolysis.

EXAMPLE 1.45

A sample of H_2SO_4 (density 1.787 g mL^{-1}) is labelled as 86% by weight. What is the molarity of acid? What volume of acid has to be used to make 1 L of 0.2 M H_2SO_4 ?

Sol. H_2SO_4 is 86% by weight.

$$\therefore \text{Weight of } \text{H}_2\text{SO}_4 = 86 \text{ g}$$

$$\text{Weight of solution} = 100 \text{ g}$$

$$\therefore \text{Volume of solution} = \frac{100}{1.787} \text{ mL} = \frac{100}{1.787 \times 1000} \text{ L}$$

$$M_{\text{H}_2\text{SO}_4} = \frac{86}{98 \times \frac{100}{1.787 \times 1000}} = 15.68$$

Let V mL of this H_2SO_4 are used to prepare 1 L of 0.2 M H_2SO_4 .

$$\therefore \text{mmoles of concentrated } \text{H}_2\text{SO}_4 = \text{mmoles of dilute } \text{H}_2\text{SO}_4$$

$$\therefore V \times 15.68 = 1000 \times 0.2$$

$$\therefore V = 12.75 \text{ mL}$$

EXAMPLE 1.46

Mole fraction of I_2 in C_6H_6 is 0.2. Calculate molality of I_2 in C_6H_6 . (M_w of $\text{C}_6\text{H}_6 = 78 \text{ g mol}^{-1}$)

Sol. $m = \frac{x_2 \times 1000}{x_1 \times M_{w1}} = \frac{0.2 \times 1000}{0.8 \times 78} = 3.205$

EXAMPLE 1.47

Calculate molality of 1 litre solution of 93% H_2SO_4 by volume. The density of solution is 1.84 g mL^{-1} .

Sol. Given H_2SO_4 is 93% by volume.

$$\therefore \text{Weight of } \text{H}_2\text{SO}_4 = 93 \text{ g}$$

$$\text{Volume of solution} = 100 \text{ mL}$$

$$\text{Weight of solution} = 100 \times 1.84 = 184 \text{ g}$$

$$\text{Weight of water} = 184 - 93 = 91 \text{ g}$$

$$\text{Molality (m)} = \frac{W_2 \times 1000}{M_{w2} \times W_1} = \frac{93 \times 1000}{98 \times 91} = 10.42$$

EXAMPLE 1.48

What would be the molality of a solution obtained by mixing equal volumes of 30% by weight H_2SO_4 ($d = 1.218 \text{ g mL}^{-1}$) and 70% by weight H_2SO_4 ($d = 1.610 \text{ g mL}^{-1}$)? If the resulting solution has density 1.425 g mL^{-1} , calculate its molality.

Sol. Let V ml of each are mixed.

For solution I

H_2SO_4 is 30% by weight.

$$\therefore \text{Weight of } \text{H}_2\text{SO}_4 = 30 \text{ g}$$

$$\text{and weight of solution} = 100 \text{ g}$$

$$\therefore \text{Volume of solution} = \frac{100}{1.218} \text{ mL}$$

$$\text{i.e., } \frac{100}{1.218} \text{ mL contains } 30 \text{ g } \text{H}_2\text{SO}_4.$$

$$\therefore V \text{ mL contains } \frac{30 \times V \times 1.218}{100} \text{ g } \text{H}_2\text{SO}_4.$$

For solution II.

H_2SO_4 is 70% by weight.

$$\therefore \text{Weight of } \text{H}_2\text{SO}_4 = 70 \text{ g}$$

$$\text{Weight of solution} = 100 \text{ g}$$

$$\therefore \text{Volume of solution} = \frac{100}{1.610} \text{ mL}$$

$$\text{i.e., } \frac{100}{1.610} \text{ mL contains } 70 \text{ g } \text{H}_2\text{SO}_4.$$

$$\therefore V \text{ mL contains } \frac{70 \times V \times 1.610}{100} \text{ g } \text{H}_2\text{SO}_4.$$

On mixing these two, total weight of H_2SO_4

$$= \left[\frac{30 \times 1.218}{100} + \frac{70 \times 1.610}{100} \right] V \text{ g} = 1.4924V \text{ g}$$

$$\text{Total volume of solution} = 2V \text{ mL}$$

$$\therefore \text{Molarity (M) of solution} = \frac{1.4924V}{98 \times \frac{2V}{1000}} = 7.61$$

Now,

$$\text{Weight of total solution} = 2V \times 1.425 \text{ g} = 2.85V \text{ g}$$

$$\therefore \text{Weight of water} = (2.85V - 1.4924V) \text{ g} \\ = 1.3576V \text{ g}$$

$$\therefore \text{Molality (m) of solution} = \frac{1.4924V}{98 \times \frac{1.3576V}{1000}} = 11.22$$

Alternatively: (use the formula)

$$d_{\text{sol}} = M \left(\frac{Mw_2}{1000} + \frac{1}{m} \right)$$

$$1.425 = 7.61 \left(\frac{98}{1000} + \frac{1}{m} \right)$$

$$\therefore m = 11.22$$

EXAMPLE 1.49

4.0 g of NaOH is contained in one decilitre of aqueous solution. Calculate the following in the solution

(d of NaOH solution = 1.038 g mL^{-1})

- Mole fraction of NaOH
- Molarity of NaOH
- Molality of NaOH

Sol. $M = \frac{W_2 \times 1000}{Mw_2 \times V_{\text{sol}}} \quad (1 \text{ decilitre} = 100 \text{ mL})$

$$= \frac{4 \times 1000}{40 \times 100} = 1$$

$$m = \frac{W_2 \times 1000}{Mw_2 \times (\text{Weight of solution} - \text{Weight of solute})}$$

$$\begin{aligned} W_1 &= \text{Weight of solvent} \\ &= \text{Weight of solution} - \text{Weight of solute} \\ &= V_{\text{sol}} \times d_{\text{sol}} - W_2 \\ &= 100 \times 1.038 - 4 = 99.8 \text{ g} \end{aligned}$$

$$\therefore m = \frac{4 \times 1000}{40 \times 99.8} = 1.002$$

$$\begin{aligned} \chi_2 &= \frac{n_2}{n_1 + n_2} = \frac{W_2 / Mw_2}{\frac{W_1}{Mw_1} + \frac{W_2}{Mw_2}} \\ &= \frac{4 / 40}{\frac{99.8}{18} + \frac{4}{40}} = \frac{0.1}{5.54 + 0.1} = 0.0177 \end{aligned}$$

EXAMPLE 1.50

Calculate the mass fraction and mole fraction of ethyl alcohol and H_2O in a solution containing 9.2 g of alcohol in 18.0 g of H_2O .

Sol. $\chi_2 = \frac{W_2 / Mw_2}{\frac{W_1}{Mw_1} + \frac{W_2}{Mw_2}}$

$$= \frac{9.2 / 46}{\frac{18}{18} + \frac{9.2}{46}} = \frac{0.2}{1 + 0.2} = 0.166 \approx 0.17$$

$$\text{Mass fraction } (X_2) = \frac{W_2}{W_1 + W_2} = \frac{9.2}{18 + 9.2}$$

$$0.338 = 0.34$$

EXAMPLE 1.51

A solution contains 410.3 g H_2SO_4 per litre of the solution at 20°C . If the density = 1.243 g mL^{-1} , what will be its molality and molarity?

Sol. $M = \frac{W_2 \times 1000}{Mw_2 \times V_{\text{sol}}}$

$$= \frac{410.3 \times 1000}{98 \times 1000} = 4.186$$

$$\begin{aligned} m &= \frac{W_2 \times 1000}{Mw_2 \times (V \times d - W_2)} \\ &= \frac{410.3 \times 1000}{98 \times (1000 \times 1.243 - 410.3)} \\ &= \frac{410.3 \times 1000}{98 \times 832.7} = 5.027 \end{aligned}$$

EXAMPLE 1.52

Concentrated HNO_3 is 69% by mass of nitric acid. Calculate the volume of the solution which contains 23 g of HNO_3 . (Density of concentrated HNO_3 solution is 1.41 g mL^{-1})

Sol. 69 g of HNO_3 = 100 g of solution

$$23 \text{ g of } \text{HNO}_3 = \frac{100}{69} \times 23 = 33.3 \text{ g}$$

$$\text{Volume of solution} = \frac{33.3}{1.41} = 23.6 \text{ mL}$$

EXAMPLE 1.53



Calculate the molality of a solution obtained by dissolving 15.87 g ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) in 168 g of H_2O .

Sol. $m = \frac{W_2 \times 1000}{Mw_2 \times W_1} = \frac{15.87 \times 1000}{46 \times 168} = 2.05$

EXAMPLE 1.54

What volume of 95% H_2SO_4 by weight ($d = 1.85 \text{ g mL}^{-1}$) and what mass of water must be taken to prepare 100 mL of 15% solution of H_2SO_4 ($d = 1.10 \text{ g mL}^{-1}$)?

Sol.

	$\xrightarrow{\text{H}_2\text{O}}$	
95%		15%
$d = 1.85$		$d = 1.10$
$V_1 = ?$		$V_2 = 100 \text{ mL}$
$M_1 V_1$	$=$	$M_2 V_2$
$\frac{95 \times 10 \times 1.85}{98} \times V_1$	$=$	$\frac{15 \times 10 \times 1.1}{98} \times 100$
$V_1 = 9.4 \text{ mL}$		
Volume of H_2O added = $100 - 9.4 = 90.6 \text{ mL}$		
Weight of H_2O added = $90.6 \times 1 = 90.6 \text{ g}$		($d_{\text{H}_2\text{O}} = 1$)

EXAMPLE 1.55

- a. Calculate the molality of a sulphuric acid solution in which the mole fraction of water is 0.85.
- b. Calculate the molality of sulphuric acid solution in which the mole fraction of water is 0.15.

Sol.

- a. Note here solvent is water, which is in excess

$$m = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}}$$

$$\chi_1 = 0.85, \chi_2 = 1 - 0.85 = 0.15$$

$$m = \frac{0.15 \times 1000}{0.85 \times 18} = 9.8$$

- b. **Note:** Here solvent is H_2SO_4 , which is in excess.

$$m = \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}} = \frac{0.15 \times 1000}{0.85 \times 98} = 1.8 \text{ m}$$

EXAMPLE 1.56

A bottle of commercial sulphuric acid

($d = 1.787 \text{ g mL}^{-1}$) is 86% by weight.

- a. What is the molarity of the acid?
- b. What volume of the acid has to be used to make 1 L of 0.2 M H_2SO_4 ?
- c. What is the molality of the acid?

Sol.

a. $M = \frac{\% \text{ by weight} \times 10 \times d}{M_{w_2}} = \frac{86 \times 10 \times 1.787}{98} = 15.68$

b. $M_1 V_1 = M_2 V_2$
 $15.68 \times V_1 = 0.2 \times 1$

$$V_1 = 0.01274 \text{ L} = 12.74 \text{ mL}$$

c. $W_1 = \text{Weight of } \text{H}_2\text{O}$
 $= \text{Weight of solution} - \text{Weight of solute}$
 $= 100 - 86 = 14 \text{ g}$

$$m = \frac{W_2 \times 1000}{M_{w_2} \times W_1}$$

$$= \frac{86 \times 1000}{98 \times 14} = 62.68$$

EXAMPLE 1.57

A 6.90 M solution of KOH contains 30% by weight of KOH. Calculate the density of the solution.

Sol. $M = \frac{\% \text{ by weight} \times 10 \times d}{M_{w_2}}$

$$6.9 = \frac{30 \times 10 \times d}{56}$$

$$d = 1.288 \text{ g mL}^{-1}$$

EXAMPLE 1.58

3.5 litre of 0.01 M NaCl is mixed with 1.5 litre of 0.05 M NaCl. What is the concentration of the final solution?

Sol. $M_1 V_1 + M_2 V_2 = M_3 V_3$

$$0.01 \times 3.5 + 0.05 \times 1.5 = M_3 \times 5$$

$$(V_3 = V_1 + V_2 = 3.5 + 1.5 = 5)$$

$$M_3 = 0.022$$

EXAMPLE 1.59

The density of 5% aqueous MgCl_2 solution is 1.043 g mL^{-1} . What is the molarity and molality of the solution? What is the molality of Cl^- ion? ($M = 24 \text{ amu}$)

Sol. M_{w_2} of $\text{MgCl}_2 = 24 + 35.5 \times 2 = 95 \text{ g}$

$$M = \frac{\% \text{ by weight} \times 10 \times d}{M_{w_2}} = \frac{5 \times 10 \times 1.043}{95} = 0.548.$$

$$\text{Weight of solvent } (W_1) = 100 - 5 = 95 \text{ g}$$

$$m = \frac{W_2 \times 1000}{M_{w_2} \times W_1} = \frac{5 \times 1000}{95 \times 95} = 0.554.$$



$$1 \text{ m} \qquad 1 \text{ m} \qquad 2 \text{ m}$$

$$0.554 \text{ m} \qquad 0.554 \text{ m} \qquad 2 \times 0.554$$

$$\therefore m \text{ of } \text{Cl}^- = 1.108 \text{ m}$$

EXAMPLE 1.60

The density of 0.06 M solution of KI in water is 1.006 g mL^{-1} . Determine the molality of this solution. ($K = 39$, $I = 127 \text{ amu}$)

Sol. M_{w_2} of KI = $39 + 127 = 166 \text{ g}$

$$d = M \left(\frac{M_{w_2}}{1000} + \frac{1}{m} \right)$$

$$1.006 = 0.006 \left(\frac{166}{1000} + \frac{1}{m} \right)$$

Solve for m ,

$$m = 0.06024$$

Alternate method:

$$M = \frac{\% \text{ by weight} \times 10 \times d}{M_{w_2}}$$

$$0.06 = \frac{\% \text{ by weight} \times 10 \times 1.006}{166}$$

$$\therefore \% \text{ by weight} = \frac{166 \times 0.06}{10 \times 1.006} = 0.99\%$$

Weight of solute = 0.99 g

Weight of solution = 100 g

Weight of solvent = 100 - 0.99 = 99.01

$$m = \frac{w_2 \times 1000}{Mw_2 \times w_1} = \frac{0.99 \times 1000}{166 \times 99} = 0.06024$$

EXAMPLE 1.61

11.2 g of carbon reacts with 21.2 litres of oxygen at 18°C and 750 mm of Hg. The cooled gases are passed through 2 litres of 2.5 N NaOH. Determine the concentration of NaOH remaining in solution which is not converted to Na_2CO_3 . Assume that CO does not react with NaOH:

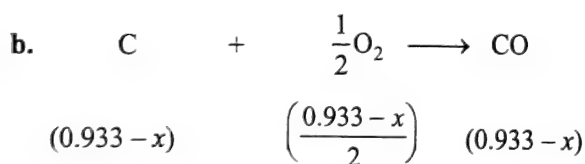
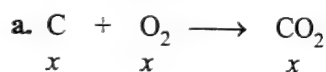
- What is the mole fraction of CO in the gases?
- What is the concentration of NaOH which is not converted to Na_2CO_3 in the remaining solution?

Sol. Mole of C = $\frac{11.2}{12} = 0.933$ mol

$$PV = nRT$$

$$\frac{750}{760} \times 21.2 = n \times 0.82 \times 291$$

$$n = \frac{750 \times 21.2}{760 \times 0.82 \times 291} = 0.876 \text{ mol of O}_2$$



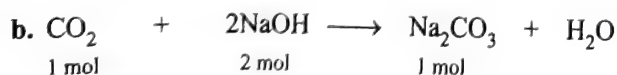
$$\text{Total moles of O}_2 = x + \frac{0.933 - x}{2} = 0.876$$

$$\therefore x = 0.821 \text{ mol}$$

$$\text{CO}_2 = 0.821 \text{ mol}$$

$$\text{CO} = 0.933 - 0.821 = 0.112 \text{ mol}$$

$$\text{a. } \therefore x_{\text{CO}} = \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2}} = \frac{0.112}{0.933} = 0.12$$



$$0.821 \text{ mol} \quad 2 \times 0.821 \text{ mol}$$

$$\text{Total moles of NaOH taken} = 2 \times 2.5 = 5 \text{ mol}$$

$$\therefore \text{Moles of NaOH} = 2 \times 0.821$$

$$\begin{aligned} \text{Moles of NaOH left} &= 5 - 2 \times 0.821 \\ &= 3.358 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Concentration of NaOH} &= \frac{\text{Moles}}{\text{Volume}} = \frac{3.358}{2} \\ &= 1.679 \text{ mol L}^{-1} \end{aligned}$$

EXAMPLE 1.62

15 mL 1 M H_2SO_4 , 25 mL of 4 M HNO_3 , and 20 mL of X M HCl were mixed and made up to 1000 mL. 20 mL of solution formed required 26 mL of $\text{Ba}(\text{OH})_2$ solution prepared by dissolving 4.725 g of pure $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in water made up to 0.25 litre. What is the molarity of HCl solution (i.e. find X).

Sol. 15 mL of 1 M H_2SO_4 + 25 mL of 4 M HNO_3 + 20 mL of X M HCl
($V_4 = 1000$ mL)

$$\therefore N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$$

$$15 \times 2 + 25 \times 4 + 20X = N_4 \times 1000$$

$$\therefore N_4 = \left(\frac{130 + 20X}{1000} \right)$$

$$\text{mEq of mixture of acid} = \text{mEq of Ba}(\text{OH})_2$$

$$Mw \text{ of Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} = 137.4 + 34 + 18 \times 8 = 315.4$$

$$Ew = \frac{315}{2} = 157.7 \text{ g}$$

$$\begin{aligned} N \text{ of Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} &= \frac{W_2 \times 1000}{Ew_2 \times V_{\text{sol}} \text{ (in mL)}} \\ &= \frac{4.725 \times 1000}{157.7 \times 250} \\ &= 0.1198 \text{ N} \approx 0.12 \text{ N} \end{aligned}$$

$$\text{mEq of acid mix} = \text{mEq of Ba}(\text{OH})_2$$

$$20 \times N_4 = 26 \times 0.12$$

$$N_4 = \frac{26 \times 0.12}{20} = 0.156 \text{ N}$$

$$\Rightarrow \frac{130 + 20X}{1000} = 0.156$$

$$\therefore X = \frac{0.156 \times 1000 - 130}{20} = 1.3$$

$$N \text{ or } M \text{ of HCl} = 1.3$$

EXAMPLE 1.63

The acid solution has a specific gravity of 1.8, when it contains 62% by weight of the acid. The solution is diluted to such an extent that its specific gravity is lowered to 1.2. What is the % by weight of the acid in the new solution.

Sol. Let 100 mL of the solution is taken

$$\text{Weight of solution} = 100 \times 1.8 = 180 \text{ g}$$

$$100 \text{ g of solution} = 62 \text{ g of acid}$$

$$180 \text{ g of solution} = \frac{62}{100} \times 180 = 111.6 \text{ g of acid}$$

$$\text{Let } x \text{ mL of H}_2\text{O} \text{ is added.}$$

$$\therefore \text{New volume} = (100 + x) \text{ mL}$$

$$\text{New weight of solution} = (180 + x) \text{ g}$$

$$(\text{Since } x \text{ mL of H}_2\text{O} = x \text{ g of H}_2\text{O}, d_{\text{H}_2\text{O}} = 1)$$

$$\therefore \text{New density} = \frac{180 + x}{100 + x}$$

$$\therefore 1.2 = \frac{180 + x}{100 + x}$$

Solving for x , we get

$$\therefore x = 300 \text{ mL} = 300 \text{ g}$$

$$\text{Weight of solution} = 180 + 300 = 480 \text{ g}$$

$$\begin{aligned} \% \text{ weight of the acid} &= \frac{W_2}{W_{\text{sol}}} \times 100 \\ &= \frac{111.6}{480} \times 100 = 23.25\% \end{aligned}$$

EXAMPLE 1.64

A solution of KCl has a density of 1.69 g mL^{-1} and is 67% by weight. Find the density of the solution if it is diluted so that the percentage by weight of KCl in the diluted solution is 30%.

Sol. Let the volume of the KCl solution be 100 mL.

$$\text{Weight of KCl solution} = 100 \times 1.69 = 169 \text{ g}$$

$$100 \text{ g of solution contains} = 67 \text{ g of KCl}$$

$$169 \text{ g of solution} = \frac{67}{100} \times 169 = 113.23 \text{ g}$$

Let x mL of H_2O be added.

$$\text{New volume of solution} = (100 + x) \text{ mL}$$

$$\text{New weight of solution} = (169 + x) \text{ g}$$

$$(\text{Since } x \text{ mL of } \text{H}_2\text{O} = x \text{ g of } \text{H}_2\text{O}, d_{\text{H}_2\text{O}} = 1)$$

$$\text{New percentage of the solution} = 30\%$$

$$\% \text{ by weight} = \frac{\text{Weight of solute} \times 100}{\text{Weight of solution}}$$

$$30 = \frac{113.23}{(169 + x)} \times 100$$

$$x = 208.43 \text{ mL} = 208.43 \text{ g}$$

$$\begin{aligned} \text{New density} &= \frac{\text{New weight of solution}}{\text{New volume of solution}} \\ &= \frac{(169 + x)}{(100 + x)} \\ &= \frac{(169 + 208.43)}{(100 + 208.43)} = \frac{377.43}{308.43} \end{aligned}$$

$$\therefore d = 1.224$$

EXAMPLE 1.65

A gaseous hydrocarbon X , was burnt in excess of oxygen. A 0.112 dm^3 sample of X , at STP gave 0.88 g of CO_2 . How many C-atoms are there in one molecule of X ?

1. 1 2. 2 3. 3 4. 4

Sol. $4. \text{C}_x\text{H}_y(\text{g}) + \left(x + \frac{y}{4}\right) \text{O}_2(\text{g}) \rightarrow x\text{CO}_2(\text{g}) + \frac{y}{2} \text{H}_2\text{O}(\text{l})$
 m moles
 $= \frac{0.112}{22.4} \times 10^3 = 5$

$$= 5x$$

Some O_2
left

$$5x$$

—

$$\therefore 5x = \frac{0.88 \times 1000}{44} = 20$$

$$\therefore x = 4$$

EXAMPLE 1.66

Ammonia is highly soluble gas in water and gives an alkaline solution of NH_4OH . What volume of NH_3 gas at STP will be required to be passed in 100 mL of 0.5 M H_2SO_4 to bring down its strength to 0.25 M ?

(For titrations with aqueous NH_3 , it is assumed that NH_4OH dissociates to 100% extent)

1. 2.24 L 2. 1.68 L 3. 1.12 L 4. 0.56 L

Sol. 3. Initially mEq of $\text{H}_2\text{SO}_4 = 100 \times 0.5 \times 2 = 100$
 mEq of H_2SO_4 required = $(0.25 \times 2) \times 100 = 50$
 mEq of H_2SO_4 used = $100 - 50$

$$= \text{mEq of } \text{NH}_4\text{OH}$$

$$= \text{mmol of } \text{NH}_4\text{OH}$$

(n factor = 1)

$$\text{mmol of } \text{NH}_3 = \text{mmol of } \text{NH}_4\text{OH} = 50$$

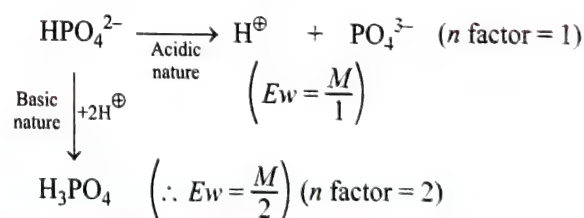
$$V_{\text{NH}_3} \text{ at STP} = 50 \times 10^{-3} \times 22.42 = 1.12 \text{ L}$$

EXAMPLE 1.67

The equivalent weight of Na_2HPO_4 can be

1. $M/2$ as base 2. $M/1$ as acid
 3. Both (a) and (b) 4. Neither (a) nor (b)

Sol. 3. $\text{Na}_2\text{HPO}_4 \longrightarrow 2\text{Na}^+ + \text{HPO}_4^{2-}$

**EXAMPLE 1.68**

Arrange the following in order of increasing masses.

- i. 1 molecule of oxygen ii. 1 atom of nitrogen
 iii. 1 mol of water iv. $1 \times 10^{-10} \text{ g}$ of iron
 1. ii < i < iii < iv 2. i < ii < iv < iii
 3. ii < i < iv < iii 4. i < ii < iii < iv

Sol. 3. i. 1 molecule of $\text{O}_2 = \frac{32}{6 \times 10^{23}}$

ii. 1 atom of N = $\frac{14}{6 \times 10^{23}}$

iii. 1 mol of $\text{H}_2\text{O} = 18 \text{ g}$

iv. Weight of Fe = 10^{-10} g

So, the order is (3).

EXAMPLE 1.69

10.1 g of KNO_3 is dissolved in 500 mL of H_2O . Mass of $\text{Ba}(\text{NO}_3)_2$ that should be added to this solution to get a molality (m) of 0.3 with respect to NO_3^- ion is

(M_w of $\text{KNO}_3 = 101 \text{ g mol}^{-1}$, M_w of $\text{Ba}(\text{NO}_3)_2 = 261 \text{ g mol}^{-1}$)

1. $\approx 1.3 \text{ g}$ 2. $\approx 13 \text{ g}$ 3. $\approx 6.5 \text{ g}$ 4. $\approx 65 \text{ g}$

Sol. 3. Moles of $\text{KNO}_3 = \text{moles of } \text{NO}_3^- = \frac{10.1}{101} = 0.1$

$$\therefore d\text{H}_2\text{O} = 1 \text{ g mL}^{-1}$$

$$\text{Weight of } \text{H}_2\text{O} = 500 \text{ mL} \times 1 = 500 \text{ g} = 0.5 \text{ kg}$$

$$m_{\text{NO}_3^-} = \frac{\text{Moles of } \text{NO}_3^-}{\text{Weight of solvent } (\text{H}_2\text{O}) \text{ in kg}} = \frac{n_{\text{NO}_3^-}}{0.5 \text{ kg}}$$

$$\Rightarrow 0.3 = \frac{n_{\text{NO}_3^-}}{0.5 \text{ kg}}, \therefore n_{\text{NO}_3^-} = 0.3 \times 0.5 = 0.15$$

(required)

$$\text{Moles of } \text{NO}_3^- \text{ obtained from } \text{KNO}_3 = 0.1$$

$$\begin{aligned} \text{Moles of } \text{NO}_3^- \text{ required from } \text{Ba}(\text{NO}_3)_2 \\ = 0.15 - 0.1 = 0.05 \end{aligned}$$

$$[2 \text{ mol of } \text{NO}_3^- \text{ is obtained from 1 mol of } \text{Ba}(\text{NO}_3)_2]$$

$$\therefore \text{Moles of } \text{Ba}(\text{NO}_3)_2 = \frac{0.05}{2}$$

$$\text{Weight of } \text{Ba}(\text{NO}_3)_2 = \frac{0.05}{2} \times 261 = 6.5 \text{ g}$$

EXAMPLE 1.70

One litre of $\text{N}/2$ HCl solution was heated in a beaker. When the volume was reduced to 600 mL, 9.125 g of HCl was lost out, the new normality of solution is

1. ≈ 0.04 2. ≈ 0.8 3. ≈ 0.4 4. ≈ 0.2

Sol. 3. $\text{HCl} \xrightarrow{\Delta} \text{HCl}$

$$0.5 \text{ N} \times 1 \text{ L} \qquad 600 \text{ mL}$$

$$= 0.5 \text{ Eq}$$

$$= 0.5 \times 36.5 \text{ g}$$

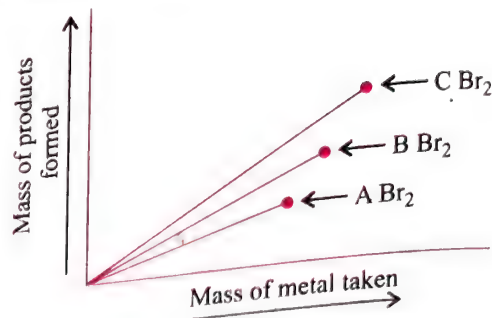
$$= 18.25 \text{ g}$$

$$\begin{aligned} \text{Mass of } \text{HCl} \text{ left after heating} &= 18.25 - 9.125 \\ &= 9.125 \text{ g} \end{aligned}$$

$$N_{\text{new}} \text{ of } \text{HCl} = \frac{9.125 \times 1000}{36.5 \times 600} = 0.416 \text{ N}$$

EXAMPLE 1.71

Three metals of alkaline earth metal group (A, B, and C) when reacted with a fixed volume of liquid Br_2 separately gave a product (metal bromides) whose mass is plotted against the mass of metals taken as shown in the figure.



From the plot, predict what relation can be concluded between the atomic weights of A, B, and C?

1. $C > B$
2. $B > A$
3. $C < A < B$
4. Data is insufficient to predict

Sol. (1, 2)

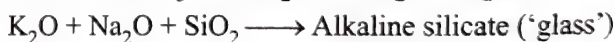
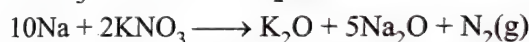
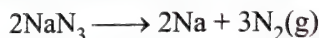
Since mass of Br_2 taken is constant, same moles of MBr_2 will be produced in each case.

$$\text{Since, moles} = \frac{\text{Mass}}{M_w}$$

The heaviest metal will produce maximum mass of product. Hence, the correct order of atomic mass of A, B, C is $A < B < C$.

EXAMPLE 1.72

The following chemical reactions used to be utilized to rapidly produce large amounts of N_2 gas inside an automobile air bag:



How many grams of KNO_3 are needed to produce enough N_2 to fill a 12.3 L air bag at 27°C and 4 atm.

1. 202 g 2. 81.25 g
3. 404 g 4. 25.25 g

Sol. 4. $PV = nRT$

$$n_{\text{N}_2} = \frac{PV}{RT} = \frac{4 \times 12.3}{0.082 \times 300} = 2 \text{ mol}$$

$$2 \text{ mol Na produces} = 3 \text{ mol } \text{N}_2$$

$$1. \text{ 10 mol Na produces} = \frac{3}{2} \times 10 = 15 \text{ mol } \text{N}_2$$

$$2. \text{ 10 mol Na} \equiv 2 \text{ mol } \text{KNO}_3 \equiv 1 \text{ mol } \text{N}_2$$

(15 mol N_2)

$$\begin{aligned} \text{Total mol of } \text{N}_2 \text{ produced} &= 15 + 1 \\ &= 16 \text{ mol } \text{N}_2 \end{aligned}$$

$$\therefore 16 \text{ mol } \text{N}_2 = 2 \text{ mol } \text{KNO}_3 \quad (M_w \text{ KNO}_3 = 101 \text{ g})$$

$$= 2 \times 101 \text{ g KNO}_3$$

$$2 \text{ mol } \text{N}_2 = \frac{2 \times 101 \times 2}{16} = 25.25 \text{ g}$$

$$\therefore \text{Weight of } \text{KNO}_3 = 25.25 \text{ g}$$

Exercises

Single Correct Answer Type

- 10 g of CaCO_3 contains
 (1) 10 moles of CaCO_3 (2) 0.1 g atom of Ca
 (3) 6×10^{23} atoms of Ca (4) 0.1 of equivalent of Ca
- A candle is burnt in a beaker until it extinguishes itself. A sample of gaseous mixture in the beaker contains 6.08×10^{20} molecules of N_2 , 0.76×10^{20} molecules of O_2 , and 0.50×10^{20} molecules of CO_2 . The total pressure is 734 mm of Hg. The partial pressure of O_2 would be
 (1) 760.0 mm of Hg (2) 76.0 mm of Hg
 (3) 7.6 mm of Hg (4) 0.76 mm of Hg
- Two glucose solutions are mixed. One has a volume of 480 mL and a concentration of 1.50 M and the second has a volume of 520 mL and concentration 1.20 M. The molarity of final solution is
 (1) 1.20 M (2) 1.50 M (3) 1.344 M (4) 2.70 M
- 1.0 g of a monobasic acid when completely acted upon Mg gave 1.301 g of anhydrous Mg salt. Equivalent weight of acid is
 (1) 35.54 (2) 36.54 (3) 17.77 (4) 18.27
- 0.1 g of metal combines with 46.6 mL of oxygen at STP. The equivalent weight of metal is
 (1) 12 (2) 24 (3) 6 (4) 36
- The vapour density of a chloride of an element is 39.5. The *Ew* of the elements is 3.82. The atomic weight of the element is
 (1) 15.28 (2) 7.64 (3) 3.82 (4) 11.46
- The *Mw* of a oxide of an element is 44. The *Ew* of the element is 14. The atomic weight of the element is
 (1) 14 (2) 28 (3) 42 (4) 56
- When 2 g of gas A is introduced into an evacuated flask kept at 25°C , the pressure was found to be 1 atmosphere. If 3 g of another gas B is then added to the same flask, the pressure becomes 1.5 atm. Assuming ideal behaviour, the ratio of molecular weights ($M_A : M_B$) is
 (1) 1:3 (2) 3:1 (3) 2:3 (4) 3:2
- How many moles of ferric alum $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ can be made from the sample of Fe containing 0.0056 g of it?
 (1) 10^{-4} mol (2) 0.5×10^{-4} mol
 (3) 0.33×10^{-4} mol (4) 2×10^{-4} mol
- Suppose elements X and Y combine to form two compounds XY_2 and X_3Y_2 when 0.1 mole of former weigh 10 g while 0.05 mole of the latter weigh 9 g. What are the atomic weights of X and Y.
 (1) 40, 30 (2) 60, 40 (3) 20, 30 (4) 30, 20
- In an experiment, 6.67 g of AlCl_3 was produced and 0.54 g Al remained unreacted. How many g atoms of Al and Cl_2 were taken originally ($\text{Al} = 27, \text{Cl} = 35.5$)?
 (1) 0.07, 0.15 (2) 0.07, 0.05
 (3) 0.02, 0.05 (4) 0.02, 0.15
- 1 g of the carbonate of a metal was dissolved in 25 mL of N-HCl. The resulting liquid required 5 mL of N-NaOH for neutralisation. The *Ew* of the metal carbonate is
 (1) 50 (2) 30 (3) 20 (4) None
- 5 mL of N-HCl, 20 mL of N/2 H_2SO_4 and 30 mL of N/3 HNO_3 are mixed together and the volume is made to 1 L. The normality of the resulting solution is
 (1) N/5 (2) N/10 (3) N/20 (4) N/40
- The *Ew* of H_3PO_4 in the reaction is

$$\text{Ca}(\text{OH})_2 + \text{H}_3\text{PO}_4 \longrightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O}$$
 ($\text{Ca} = 40, \text{P} = 31, \text{O} = 16$)
 (1) 49 (2) 98 (3) 32.66 (4) 147
- A gaseous mixture contains O_2 and N_2 in the ratio of 1:4 by weight. The ratio of their number of molecules is
 (1) 1:4 (2) 1:8 (3) 7:32 (4) 3:16
- If 0.5 mole of BaCl_2 is mixed with 0.20 mole of Na_3PO_4 , the maximum number of moles of $\text{Ba}_3(\text{PO}_4)_2$ then can be formed is
 (1) 0.1 (2) 0.2 (3) 0.5 (4) 0.7
- Upon mixing 50.0 mL of 0.1 M lead nitrate solution with 50 mL of 0.05 M chromic sulphate solution, precipitation of lead sulphate solution takes place. How many moles of lead sulphate are formed and what is the molar concentration of chromic sulphate left in the solution?
 (1) 0.005, 0.0084 (2) 0.0084, 0.005
 (3) 0.005, 0.00084 (4) 0.05, 0.00084
- The melting point of a substance was quoted as 52.5°C , 52.57°C , 52.571°C , and 52.5713°C . Which of these values would be most acceptable and which will have maximum uncertainty?
 (1) 52.5°C (2) 52.57°C
 (3) 52.571°C (4) 52.5713°C
- What weight of a metal of equivalent weight 12 will give 0.475 g of its chloride?
 (1) 0.12 g (2) 0.24 g (3) 0.36 g (4) 0.48 g
- 4.2 g of a metallic carbonate MCO_3 was heated in a hard glass tube and CO_2 evolved was found to have 1120 mL of volume at STP. The *Ew* of the metal is
 (1) 12 (2) 24 (3) 18 (4) 15

21. If 0.5 g of a mixture of two metals A and B with respective equivalent weights 12 and 9 displace 560 mL of H_2 at STP from an acid, the composition of the mixture is
 (1) 40% A, 60% B (2) 60% A, 40% B
 (3) 30% A, 70% B (4) 70% A, 30% B
22. What is the valency of an element of which the equivalent weight is 12 and the specific heat is 0.25?
 (1) 1 (2) 2 (3) 3 (4) 4
23. The mineral rutile is an oxide of titanium containing 39.95% oxygen and is isomorphous with cassiterite (SnO_2). The atomic weight of titanium is
 (1) 68.10 (2) 58.10 (3) 48.10 (4) 38.10
24. 13.4 g of a sample of unstable hydrated salt $Na_2SO_4 \cdot xH_2O$ was found to contain 6.3 g of H_2O . The number of molecules of water of crystallisation is
 (1) 5 (2) 7 (3) 2 (4) 10
25. One litre of 0.15 M HCl and one litre of 0.3 M HCl is given. What is the maximum volume of 0.2 M HCl which one can make from these two solutions? No water is added.
 (1) 1.2 L (2) 1.5 L (3) 1.3 L (4) 1.4 L
26. The normality of a solution that results from mixing 4 g of NaOH, 500 mL of 1 M HCl, and 10.0 mL of H_2O_4 (specific gravity 1.1, 49% H_2SO_4 by weight) is
 (The total volume of solution was made to 1 L with water)
 (1) 0.51 (2) 0.71 (3) 1.02 (4) 0.45
27. A certain compound has the molecular formula X_4O_6 . If 10 g of X_4O_6 has 5.72 g X, the atomic mass of X is
 (1) 32 amu (2) 37 amu (3) 42 amu (4) 98 amu
28. 5.6 g of a metal forms 12.7 g of metal chloride. Hence equivalent weight of the metal is
 (1) 127 (2) 254 (3) 56 (4) 28
29. The molarity of H_2SO_4 is 18 M. Its density is 1.8 g mL^{-1} . Hence, molality is:
 (1) 36 (2) 200 (3) 500 (4) 18
30. 10 L of hard water required 0.56 g of lime (CaO) for removing hardness. Hence, temporary hardness in ppm (part per million 10^6) of $CaCO_3$ is:
 (1) 100 (2) 200 (3) 10 (4) 20
31. How many grams of phosphoric acid would be needed to neutralise 100 g of magnesium hydroxide? (The molecular weights are: $H_3PO_4 = 98$ and $Mg(OH)_2 = 58.3$)
 (1) 66.7 g (2) 252 g (3) 112 g (4) 168 g
32. The simplest formula of a compound containing 50% of an element X (atomic weight 10) and 50% of element Y (atomic weight 20) is:
 (1) XY (2) X_2Y (3) XY_2 (4) X_2Y_3
33. When 10 mL of ethyl alcohol (density 0.7893 g mL^{-1}) is mixed with 20 mL of water (density 0.9971 g mL^{-1}) at 25°C , the final solution has a density of 0.9571 g mL^{-1} . The percentage change in total volume on mixing is
 (1) 3.1% (2) 2.4%
 (3) 1% (4) None of these
34. The molality of 1 L solution with $x\%$ H_2SO_4 is equal to 9. The weight of the solvent present in the solution is 910 g. The value of x is:
 (1) 90 (2) 80.3 (3) 40.13 (4) 9
35. The density of 1 M solution of NaCl is 1.0585 g mL^{-1} . The molality of the solution is
 (1) 1.0585 (2) 1.00 (3) 0.10 (4) 0.0585
36. 100 mL of mixture of NaOH and Na_2SO_4 is neutralised by 10 mL of 0.5 M H_2SO_4 . Hence, NaOH in 100 mL solution is
 (1) 0.2 g (2) 0.4 g (3) 0.6 g (4) None
37. An organic compound contains 4% sulphur. Its minimum molecular weight is
 (1) 200 (2) 400 (3) 800 (4) 1600
38. A gaseous mixture contains oxygen and nitrogen in the ratio 1:4 by weight. Therefore, the ratio of the number of molecules is:
 (1) 1:4 (2) 1:8 (3) 7:32 (4) 3:16
39. 0.116 g of $C_4H_4O_4$ (A) is neutralised by 0.074 g of $Ca(OH)_2$. Hence, protonic hydrogen (H^+) in (A) will be
 (1) 1 (2) 2 (3) 3 (4) 4
40. A hydrate of Na_2SO_3 has 50% water by mass. It is
 (1) $Na_2SO_3 \cdot 5H_2O$ (2) $Na_2SO_3 \cdot 6H_2O$
 (3) $Na_2SO_3 \cdot 7H_2O$ (4) $Na_2SO_3 \cdot 2H_2O$
41. 10 g mixture of $NaHCO_3$ and Na_2CO_3 has 1.68 g $NaHCO_3$. It is heated at 400 K. Weight of the residue will be
 (1) 9.38 g (2) 8.32 g (3) 10.0 g (4) 1.68 g
42. Mole fraction of ethanol in ethanol water mixture is 0.25. Hence, the percentage concentration of ethanol by weight of mixture is
 (1) 25% (2) 75% (3) 46% (4) 54%
43. $N_2 + 3H_2 \longrightarrow 2NH_3$
 Molecular weight of NH_3 and N_2 are x_1 and x_2 , respectively. Their equivalent weights are y_1 and y_2 , respectively. Then $(y_1 - y_2)$ is
 (1) $\left(\frac{2x_1 - x_2}{6}\right)$ (2) $(x_1 - x_2)$
 (3) $(3x_1 - x_2)$ (4) $(x_1 - 3x_2)$
44. How many moles of electrons weigh one kilogram?
 (1) 6.023×10^{23} (2) $\frac{1}{9.108} \times 10^{31}$
 (3) $\frac{6.023}{9.108} \times 10^{54}$ (4) $\frac{1}{9.108 \times 6.023} \times 10^8$
45. The weight of 1×10^{22} molecules of $CuSO_4 \cdot 5H_2O$ is
 (1) 4.14 g (2) 5.14 g (3) 6.14 g (4) 7.14 g

46. How many moles of O_2 will be liberated by one mole of CrO_5 is the following reaction:



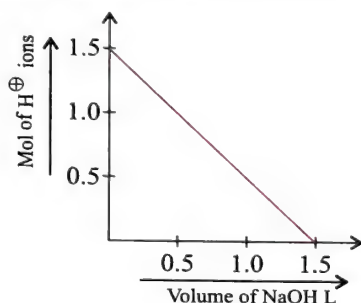
- (1) 4.5 (2) 2.5 (3) 1.25 (4) None

47. $BrO_3^- + 5Br^- \longrightarrow Br_2 + 3H_2O$

If 50 mL 0.1 M BrO_3^- is mixed with 30 mL of 0.5 M Br^- solution that contains excess of H^+ ions, the moles of Br_2 formed are

- (1) 6.0×10^{-4} (2) 1.2×10^{-4}
(3) 9.0×10^{-3} (4) 1.8×10^{-3}

48. To 1 L of 1.0 M impure H_2SO_4 sample, 1.0 M NaOH solution was added and a plot was obtained as follows:



The % purity of H_2SO_4 and the slope of curve, respectively, are:

- (1) 75%, $-1/2$ (2) 75%, -1
(3) 50%, $-1/3$ (4) 50%, $-1/4$

49. The expression relating mole fraction of solute (x_2) and molarity (M) of the solution is: (where d is the density of the solution in $g L^{-1}$ and Mw_1 and Mw_2 are the molar masses of solvent and solute, respectively)

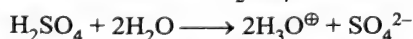
$$(1) x_2 = \frac{M \times Mw_1}{M(Mw_1 - Mw_2) + 1000d}$$

$$(2) x_2 = \frac{M \times Mw_1}{M(Mw_1 - Mw_2) + d}$$

$$(3) x_2 = \frac{M \times Mw_1}{M(Mw_1 - Mw_2) - 1000d}$$

$$(4) x_2 = \frac{M \times Mw_1}{M(Mw_1 - Mw_2) - d}$$

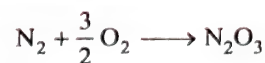
50. Consider the ionisation of H_2SO_4 as follow:



The total number of ions furnished by 100 mL of 0.1 M H_2SO_4 will be

- (1) 1.2×10^{23} (2) 0.12×10^{23} (3) 0.18×10^{23}
(4) 1.8×10^{23}

51. Calculate the number of oxygen atoms required to combine with 7.0 g of N_2 to form N_2O_3 if 80% of N_2 is converted into products.



- (1) 3.24×10^{23} (2) 3.6×10^{23}
(3) 18×10^{23} (4) 6.02×10^{23}

52. 36.5% HCl has density equal to $1.20 g mL^{-1}$. The molarity (M) and molality (m), respectively, are

- (1) 15.7, 15.7 (2) 12, 12
(3) 15.7, 12 (4) 12, 15.7

53. 10 mL of 1 M $BaCl_2$ solution and 5 mL 0.5 M K_2SO_4 are mixed together to precipitate out $BaSO_4$. The amount of $BaSO_4$ precipitated will be

- (1) 0.005 mol (2) 0.00025 mol
(3) 0.025 mol (4) 0.0025 mol

54. Mole fraction of a solute in an aqueous solution is 0.2. The molality of the solution will be

- (1) 13.88 (2) 1.388
(3) 0.138 (4) 0.0138

55. An excess of NaOH was added to 100 mL of a $FeCl_3$ solution which gives 2.14 g of $Fe(OH)_3$. Calculate the normality of $FeCl_3$ solution.

- (1) 0.2 N (2) 0.3 N
(3) 0.6 N (4) 1.8 N

56. Two samples of HCl of 1.0 M and 0.25 M are mixed. Find volumes of these samples taken in order to prepare 0.75 M HCl solution. Assume no water is added

- (I) 20 mL, 10 mL (II) 100 mL, 50 mL
(III) 40 mL, 20 mL (IV) 50 mL, 25 mL
(1) I, II, IV (2) I, II (3) II, III, IV (4) I, II, III, IV

57. If 100 mL of H_2SO_4 and 100 mL of H_2O are mixed, the mass percent of H_2SO_4 in the resulting solution is ($d_{H_2SO_4} = 0.09 g mL^{-1}$, $d_{H_2O} = 1.0 g mL^{-1}$)

- (1) 90 (2) 47.36 (3) 50 (4) 60

58. 12.5 mL of a solution containing 6.0 g of a dibasic acid in 1 L was found to be neutralized by 10 mL of a decinormal solution of NaOH. The molecular weight of the acid is

- (1) 150 (2) 120 (3) 110 (4) 75

59. One litre of a sample of hard water contains 5.55 mg of $CaCl_2$ and 4.75 mg of $MgCl_2$. The total hardness in terms of ppm of $CaCO_3$ is

- (1) 5 ppm (2) 10 ppm
(3) 20 ppm (4) None of these

60. 10 mL of 0.2 N HCl and 30 mL of 0.1 N HCl together exactly neutralise 40 mL of solution of NaOH, which is also exactly neutralised by a solution in water of 0.61 g of an organic acid. What is the equivalent weight of the organic acid?

- (1) 61 (2) 91.5 (3) 122 (4) 183

Multiple Correct Answers Type

Laws of Chemical Combination

- Which of the statements are correct?
 - Physical quantity represented by work in joule is $\text{kg m}^2 \text{s}^{-2}$.
 - Physical quantity represented by force in newton is kg m s^{-2} .
 - Physical quantity represented by work in joule is kg m s^{-2} .
 - Physical quantity represented by force in newton is $\text{kg m}^2 \text{s}^{-2}$.
- Which of the statements are false?
 - Physical quantity represented by volume is dm^3 .
 - The length of pencil is 5 cms.
 - The work done by a system is 5 Joules.
 - Air sometimes is considered as a heterogeneous mixture due to the presence of dust particles which form a separate phase.
- Which of the statements are true?
 - Law of constant composition is true for all types of compounds.
 - Molar volume of a gas at standard conditions is 22.4 L.
 - Vapour density of a gas is twice of its molecular mass.
 - Atomic masses of most elements are fractional.
- Which of the statements are true?
 - The equivalent weight of $\text{Ca}_3(\text{PO}_4)_2$ is $M_w/6$.
 - The equivalent weight of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ is $M_w/3$.
 - The equivalent weight of K_2SO_4 is $M_w/2$.
 - The equivalent weight of potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is $M_w/8$.

where M_w is the molecular weight of the respective compounds.
- Which of the statements are true?
 - Brass is an element.
 - Dry ice is a mixture.
 - Aerated drink, e.g., coca cola, is a mixture.
 - Diesel is a mixture.
- Two bulbs A and B contain 16 g O_2 and 16g O_3 , respectively. Which of the statements are true?
 - Both bulbs contain same number of atoms.
 - Both bulbs contain different number of atoms.
 - Both bulbs contain same number of molecules.
 - Bulb A contains $N_A/2$ molecules while bulb B contains $N_A/3$ molecules. (N_A = Avogadro's number).
- A bulb contains 1.6 g of O_2 . It contains.
 - 0.05 mol of O_2
 - 3.011×10^{22} molecules of O_2
 - 1.12 L of O_2 at STP
 - 1.22 L of O_2 at SATP
- Which of the following have same significant figures?
 - 0.070
 - 0.70
 - 7.0
 - 70
- Which of the following have same significant figures?
 - 6.02×10^{23}
 - 7.70×10^{-20}
 - 7.50
 - 0.75
- Which of the following relations are correct?
 - 1 eV = 9.11×10^{-4} J
 - 1 L = 1 dm^3
 - 1 J = 1.98 cal
 - 1 atm = 1.01325 bar
- Which of the following statements are correct?
 - French chemist A. Lavoisier is called the father of chemistry and proposed the law of conservation of mass.
 - French chemist Joseph Proust proposed the law of definite proportions.
 - Dalton proposed the law of multiple proportions.
 - Richter proposed the law of reciprocal proportions.
- Which of the statements are true about the law of chemical combination?
 - Potassium combines with two isotopes of chlorine (^{35}Cl and ^{37}Cl) to form two samples of KCl. Their formation follows the law of definite composition.
 - Different proportions of oxygen in the various oxides of sulphur prove the law of multiple proportions.
 - H_2O and H_2S contain 11.11% hydrogen and 5.88% hydrogen, respectively, whereas SO_2 contains 50% sulphur. The above data prove the law of reciprocal proportions.
 - In the decomposition of NH_3 , $(2\text{NH}_3 \xrightarrow{\Delta} \text{N}_2 + 3\text{H}_2)$, the ratio of volumes of NH_3 , N_2 , and H_2 is 2:1:3. The above data proves the Gay Lussac law.
- Which of the following statements are wrong?
 - 1.6 g of a hydrocarbon on combustion in excess of oxygen produces 1.2 of CO_2 and 0.4 of H_2O . The data illustrates the law of conservation of mass.
 - The product of atomic mass and specific heat of any elements is a constant and is approximately 6.4. This is known as Dulong Petit's law.
 - The atomic masses of the elements are usually fractional because they are mixtures of allotropes.
 - The best standard of atomic mass is hydrogen-1.008.
- Which of the following pair of compounds illustrate the law of multiple proportions?
 - SO_2 and SO_3
 - NO_2 and N_2O
 - MgO and $\text{Mg}(\text{OH})_2$
 - NO and N_2O_5
- Which of the following statements are correct?
 - A sample of CaCO_3 contains Ca = 40%, C = 12%, and O = 48%. If the law of constant composition is true,

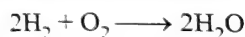
then the mass of Ca in 10 g of CaCO_3 from another source is 4.0 g.

- (2) 12 g of carbon is heated in vacuum and there is no change in the mass, is the best example of the law of conservation of mass.
- (3) Air is heated at constant pressure and there is no change in mass but the volume increases, is the best example of the law of conservation of mass.
- (4) SO_2 gas was prepared by (i) heating Cu with conc H_2SO_4 , (ii) burning sulphur in oxygen, (iii) reacting sodium sulphite (Na_2SO_3) with dilute H_2SO_4 . It was observed that in each case, S and O combine in the ratio of 1:1. This data illustrates the law of constant composition.

Limiting Reagent

16. Which of the following statements is/are correct?

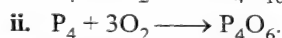
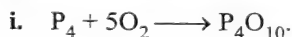
A mixture containing 64.0 g H_2 and 64.0 g O_2 is ignited so that water is formed as follows:



- (1) H_2 is the limiting reagent
- (2) O_2 is the limiting reagent.
- (3) The reaction mixture contains 72.0 g of H_2O and 56.0 g of unreacted H_2 .
- (4) The reaction mixture contains 56.0 g of H_2O and 72.0 g of unreacted H_2 .

17. Which of the following statements is/are wrong?

The following reactions occur:

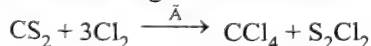


1.24 g of P_4 reacts with 8.0 g of O_2 .

- (1) P_4 is the limiting quantity.
- (2) O_2 is the limiting quantity.
- (3) Mass of P_4O_{10} obtained is 2.2 g.
- (4) Mass of P_4O_6 obtained is 2.84 g.

18. Which of the following is/are correct.

The following reaction occurs:

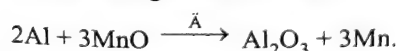


1.0 g of CS_2 and 2.0 g of Cl_2 reacts.

- (1) 0.714 g CS_2 is used in the reaction.
- (2) 0.286 g CS_2 is in excess.
- (3) 1.45 g of CCl_4 is formed.
- (4) 0.8 g Cl_2 is in excess.

19. Which of the following statements is/are correct?

The following reaction occurs:



108.0 g of Al and 213.0 g of MnO was heated to initiate the reaction. (M_w of MnO = 71, atomic weight of Al = 13)

- (1) Al is present in excess.
- (2) MnO is present in excess.

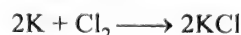
- (3) 54.0 g of Al is required.
- (4) 159.0 g of MnO is in excess.

20. Which of the following statements is/are correct?

- i. 21.0 of lithium reacts with 32.0 g of O_2 .



- ii. 3.9 g of K reacts with 4.26 g of Cl_2 .

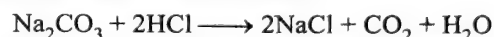


[Atomic weight of Li = 7 and K = 39. M_w of Li_2O = 30 and KCl = 74.5 g mol^{-1}]

- (1) In reaction (i), O_2 is in excess.
- (2) 45.0 g of Li_2O is formed in reaction (i).
- (3) In reaction (ii), Cl_2 is in excess.
- (4) 7.45 g of KCl is formed in reaction (ii).

21. Which of the following is/are correct?

The following reaction occurs:



106.0 g of Na_2CO_3 reacts with 109.5 g of HCl.

- (1) The HCl is in excess.
- (2) 117.0 g of NaCl is formed.
- (3) The volume of CO_2 produced at 1 bar and 273 K is 22.7 L.
- (4) The volume of CO_2 produced at 1 bar and 298 K is 24.7 L.

22. Equal weights of X (atomic weight = 36) and Y (atomic weight = 24) are reacted to form the compound X_2Y_3 , which of the following is/are correct?

- (1) X is the limiting reagent.
- (2) Y is the limiting reagent.
- (3) No reactant is left over.
- (4) Mass of X_2Y_3 formed is double the mass of X taken.

Mole Concept in Solution

23. Which of the following solutions contains approximately equal hydrogen ion concentration?

- (1) 100 mL of 0.1 M HCl + 50 mL H_2O
- (2) 75 mL of 0.1 M HCl + 75 mL H_2O
- (3) 50 mL of 0.1 M H_2SO_4 + 100 mL H_2O
- (4) 100 mL of 0.1 N H_2SO_4 + 50 mL H_2O

24. Which of the following solutions contains same molar concentration?

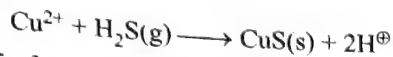
- (1) 166 g. KI/L solution.
- (2) 33.0 g $(\text{NH}_4)_2\text{SO}_4$ in 200 mL solution
- (3) 25.0 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 mL solution
- (4) 27.0 mg Al^{3+} per mL solution.

25. Which of the following has equal mass of Cl^- ions in 1.0 L of each of the following solutions?

- (1) 5% NaCl (density = 1.07 g mL^{-1})
- (2) 5% KCl ($d = 1.06$ g mL^{-1})
- (3) 58.5 g NaCl
- (4) 55.5 g BaCl_2

26. Which of the following statements is/are correct?

Excess of $\text{H}_2\text{S}(\text{g})$ is bubbled into 1.0 L of 0.1 M CuCl_2 solution.



- (1) 9.55 of CuS is produced.
 - (2) The concentration of H^{\oplus} ions is 0.2 M
 - (3) The concentration of H^{\oplus} ions is 0.1 M.
 - (4) 95.5 g CuS is produced
27. Which of the following statements is/are correct?
- 20.0 mL of 6.0 M HCl is mixed with 50.0 mL of 2.0 M $\text{Ba}(\text{OH})_2$, and 30 mL of water is added.
- (1) The concentration of OH^{\ominus} remaining in solution is 0.8 M.
 - (2) The concentration of Cl^{\ominus} remaining in solution is 1.2 M.
 - (3) The concentration of Ba^{2+} remaining in solution is 1.0 M
 - (4) 80 mmol of OH^{\ominus} is in excess.
28. Which of the following is/are correct?
- 100 mL of 3.0 M HClO_3 reacts with excess of $\text{Ba}(\text{OH})_2$ according to the equation:
- $$\text{Ba}(\text{OH})_2 + 2\text{HClO}_3 \longrightarrow \text{Ba}(\text{ClO}_3)_2 + 2\text{H}_2\text{O}$$
- (Mw of $\text{Ba}(\text{ClO}_3)_2 = 304 \text{ g mol}^{-1}$)
- (1) 1.5 mol of $\text{Ba}(\text{ClO}_3)_2$ is formed.
 - (2) 3 mol of $\text{Ba}(\text{ClO}_3)_2$ is formed.
 - (3) 45.6 g of $\text{Ba}(\text{ClO}_3)_2$ is obtained.
 - (4) 4.56 g of $\text{Ba}(\text{ClO}_3)_2$ is obtained.
29. An excellent solution for cleaning grease stains from cloth or leather consists of the following components: CCl_4 (80% by volume), ligroin (16%), and amyl alcohol (4%). How many mL of each should be taken to make up 80 mL of solution?
- (1) 64 mL CCl_4
 - (2) 12.8 mL ligroin
 - (3) 32 mL of amyl alcohol
 - (4) 3.2 mL of amyl alcohol
30. Which of the following statements is/are correct?
- (1) Mass of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ needed to make up 100 mL of an aqueous solution of concentration 27.0 mg of Al^{3+} per mL is 33.3 g.
(Mw of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} = 666 \text{ g mol}^{-1}$, atomic weight of $\text{Al} = 27 \text{ g}$).
 - (2) Mass of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ($M_w = 266.5 \text{ g}$) needed to prepare 1.0 L solution containing 26.0 g Cr^{3+} per litre is 133.25 g. (Atomic weight of $\text{Cr} = 52 \text{ g}$)

- (3) Mass of NH_4Cl needed to prepare 100 mL of a solution containing 80 mg NH_4Cl per mL is 8.0 g.

- (4) Mass of NH_3 per mL of solution needed for solution of NH_3 in water containing 20% NH_3 by weight (density $= 0.8 \text{ g mL}^{-1}$) is 0.16 g mL^{-1} .

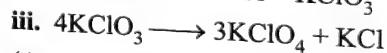
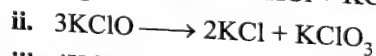
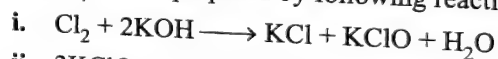
31. 100 mL of 0.06 M $\text{Ca}(\text{NO}_3)_2$ is added to 50 mL of 0.06 M $\text{Na}_2\text{C}_2\text{O}_4$. After the reaction is complete.

- (1) 0.003 moles of calcium oxalate will get precipitated.
- (2) 0.003 M of excess Ca^{2+} will remain in excess.
- (3) $\text{Na}_2\text{C}_2\text{O}_4$ is the limiting reagent.
- (4) $\text{Ca}(\text{NO}_3)_2$ is the excess reagent.

32. If 100 mL of 1 M H_2SO_4 solution is mixed with 100 mL of 98% (W/W) of H_2SO_4 solution ($d = 0.1 \text{ g mL}^{-1}$), then

- (1) Concentration of solution becomes half.
- (2) Volume of solution becomes 200 mL.
- (3) Mass of H_2SO_4 in the solution is 98 g.
- (4) Mass of H_2SO_4 in the solution is 19.6 g.

33. KClO_4 can be prepared by following reactions:



(Atomic weight of K, Cl, and O are 39, 35.5, and 16)

- (1) The amount of Cl_2 required to prepare 277 g of KClO_4 by above series of reaction is 568 g.
- (2) The volume of KOH in litres used by Cl_2 , if KOH is 1.5 M, is 1.067 L.
- (3) The amount of Cl_2 required to prepare 200 g of KClO_4 by above series of reaction is 284 g.
- (4) The volume of KOH in litres used by Cl_2 , if KOH is 1.5 M, is 10.67 L.

34. When 100 mL of 0.1 M KNO_3 and 400 mL of 0.2 M HCl and 500 mL of 0.3 M H_2SO_4 are mixed, then in the resulting solution

- (1) The molarity of $\text{K}^{\oplus} = 0.01 \text{ M}$
- (2) The molarity of $\text{SO}_4^{2-} = 0.15 \text{ M}$
- (3) The molarity of $\text{H}^{\oplus} = 0.38 \text{ M}$
- (4) The molarity of $\text{NO}_3^{\ominus} = 0.08$ and $\text{Cl}^{\ominus} = 0.01 \text{ M}$

35. 100 g sample of clay (containing 19% H_2O , 40% silica, and inert impurities as rest) is partially dried so as to contain 10% H_2O .

Which of the following is/are correct statement(s)?

- (1) The percentage of silica in it is 44.4 %.
- (2) The mass of partially dried clay is 90.0 g.
- (3) The percentage of inert impurity in it is 45.6%.
- (4) The mass of water evaporated is 10.0 g.

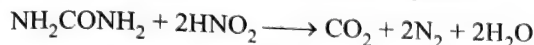
36. In which of the following pairs, 10 g of each have an equal number of molecules?

- (1) N_2O and CO
- (2) N_2 and C_3O_2
- (3) N_2 and CO
- (4) N_2O and CO_2

Linked Comprehension Type

Paragraph 1

A sample of urine containing 0.3 g of urea was treated with an excess of 0.2 M nitrous acid, according to the equation.



The gases produced are passed through aqueous KOH solution and the final volume is measured.

(Given, $M_{w,\text{urea}} = 60 \text{ g mol}^{-1}$, molar volume of gas at standard condition, i.e., at room temperature 25°C and 1 atm pressure. RTP (room temperature pressure) also is 24.4 L or $24400 \text{ mL mol}^{-1}$)

1. What is the volume at RTP?

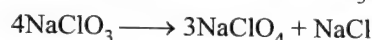
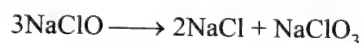
- (1) 122 mL (2) 244 mL (3) 366 mL (4) 488 mL

2. What is the volume of HNO_2 consumed by urea?

- (1) 12.5 mL (2) 25 mL (3) 50 mL (4) 75 mL

Paragraph 2

Consider the following series of reactions:



3. How much Cl_2 is needed to prepare 122.5 g NaClO_4 by above sequence?

- (1) 284.0 g (2) 213.0 g
(3) 142.0 g (4) 71.0 g

4. How much Cl_2 is needed to prepare 106.5 g of NaClO_3 by the above sequence?

- (1) 284.0 g (2) 213.0 g
(3) 142.0 g (4) 71.0 g

Paragraph 3

The percentage labelling of oleum (mixture of H_2SO_4 and SO_3) refers to the total mass of pure H_2SO_4 . The total amount of H_2SO_4 found after adding calculated amount of water to 100 g oleum is the percentage labelling of oleum. The higher the percentage labelling of oleum higher is the amount of free SO_3 in the oleum sample.

5. What is the amount of free SO_3 in an oleum sample labelled as '118%'.

- (1) 40% (2) 50% (3) 70% (4) 80%

6. The percent free SO_3 in an oleum is 20%. Label the sample of oleum in terms of percent H_2SO_4 .

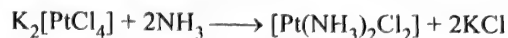
- (1) 113.5% (2) 104.5% (3) 106.75% (4) 120%

7. 100 g sample of '147 %' oleum was taken and calculated amount of H_2O was added to make H_2SO_4 . 500 mL solution of $x \text{ M}$ KOH solution is required to neutralise the solution. The value of x is.

- (1) 1 M (2) 2 M (3) 4 M (4) 6 M

Paragraph 4

Cisplatin is used as an anticancer agent for the treatment of solid tumors, and it is prepared as follows:



Potassium tetra

Cisplatin

chloro platinate (II)

Given 83.0 g of $\text{K}_2[\text{PtCl}_4]$ is reacted with 83.0 g of NH_3 .

[Atomic weights: K = 39, Pt = 415, Cl = 35.5, N = 14]

8. Which reactant is the limiting reagent and which is in excess?

Limiting

Excess

(1) $\text{K}_2[\text{PtCl}_4]$

NH_3

(2) NH_3

$\text{K}_2[\text{PtCl}_4]$

(3) None

None

(4) Both

Both

9. The number of mol of $\text{K}_2[\text{PtCl}_4]$ and NH_3 used, respectively, are

- (1) 0.1, 0.2 (2) 0.2, 0.4 (3) 0.3, 0.6 (4) 0.03, 0.06

10. The number of mol of excess reactant is

- (1) 4.68 (2) 4.78 (3) 4.58 (4) 4.48

Paragraph 5

Salt cake (Na_2SO_4) is prepared as follows:



11. How much salt cake could be produced from 100.0 g of 90% pure salt in the above reaction?

- (1) 109.8 g (2) 54.9 g (3) 36.6 g (4) 209.8 g

12. How much 80% pure salt cake could be produced from 100.0 g of 90% pure salt in the above reaction?

- (1) 43.92 g (2) 68.62 g (3) 87.84 g (4) 137.25 g

Matrix Match Type

1. Match the items given in column I with those in column II.

	Column I		Column II
a.	What mass of $(\text{NH}_4)_2\text{CO}_3$ ($M_w = 96 \text{ g mol}^{-1}$) contains 0.4 mol NH_4^+ ?	p.	1.92 g
b.	Mass of $(\text{NH}_4)_2\text{CO}_3$ which contains 6.02×10^{23} hydrogen atoms	q.	19.2 g
c.	Mass of $(\text{NH}_4)_2\text{CO}_3$ which will produce 3.0 mL of CO_2 when treated with sufficient acid.	r.	12.0 g
d.	Mass of $(\text{NH}_4)_2\text{CO}_3$ is required to prepare 100 mL of 0.2 M $(\text{NH}_4)_2\text{CO}_3$ solution.	s.	288.0 g

2. Match the solution mixtures given in column I with the concentrations given in column II.

Column I	Column II
a. 11.1 g CaCl_2 and 29.25 g of NaCl are diluted with water to 100 mL	p. $[\text{Ca}^{2+}] = 0.8 \text{ M}$ $[\text{Na}^+] = 1.2 \text{ M}$ $[\text{Cl}^-] = 2.8 \text{ M}$
b. 3.0 L of 4.0 M NaCl and 4.0 L of 2.0 M CaCl_2 are combined and diluted to 10.0 L	q. $[\text{Ca}^{2+}] = 0.001 \text{ M}$ $[\text{Na}^+] = 0.005 \text{ M}$ $[\text{Cl}^-] = 0.007 \text{ M}$
c. 300 mL of 3.0 M NaCl is added to 200 mL of 4.0 M CaCl_2	r. $[\text{Ca}^{2+}] = 1.6 \text{ M}$ $[\text{Na}^+] = 1.8 \text{ M}$ $[\text{Cl}^-] = 5.0 \text{ M}$
d. 100 mL of 2.0 M HCl + 200 mL of 1.0 M NaOH + 150 mL of 4.0 M CaCl_2 + 50 mL of H_2O	s. $[\text{Ca}^{2+}] = 1.2 \text{ M}$ $[\text{Na}^+] = 0.4 \text{ M}$ $[\text{Cl}^-] = 2.8 \text{ M}$

3. Match the items given in column I with those in column II.

Column I	Column II
a. Molarity (M)	p. Temperature
b. Molality (m)	q. Dilution
c. Mole fraction (χ)	r. volume
d. Normality (N)	

4. Match the weight of reactants given in column I with weight of products marked (?) given in column II.

Column I	Column II
a. $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ 1.0 g 1.0 g ?	p. 0.56 g
b. $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$ 1.0 g 1.0 g ?	q. 1.333 g
c. $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$ 1.0 g ?	r. 1.125 g
d. $\text{C} + 2\text{H}_2 \longrightarrow \text{CH}_4$ 1.0 g 1.0 g ?	s. 1.214 g

5. Match the amount of reactants given in column I with neutralisation reactions given in column II.

Column I	Column II
a. 4.9 g H_2SO_4	p. 200 mL of 0.5 N NaOH is used for complete neutralisation
b. 4.9 g of H_3PO_4	q. 200 mmol oxygen atoms
c. 4.5 g of $\text{H}_2\text{C}_2\text{O}_4$	r. Central atom has its highest oxidation state.

d. 5.3 g Na_2CO_3	s. May react with an oxidising agent.
	t. Shape and geometry around the central atom is same

6. Match the items given in column I with those in column II.

Column I	Column II
a. 9.8% H_2SO_4 by weight (density = 1.8 g mL^{-1})	p. 3.6 N
b. 9.8% H_3PO_4 by weight (density = 1.2 g mL^{-1})	q. 1.2 M
c. $1.8 N_A$ molecules of HCl is 500 mL	r. 1.8 Equivalents
d. 250 mL of 4N NaOH + 250 mL of 1.6 M Ca(OH)_2	s. 1.10 m

7. Match the items given in column I with those in column II.

Column I	Column II
a. 15.8 g KMnO_4	p. 6.023×10^{22} molecules
b. 9.0 g $\text{H}_2\text{C}_2\text{O}_4$	q. 24.092×10^{22} atoms of oxygen
c. 8.8 g CO_2	r. 0.1 mol
d. 5.6 g CO	s. 0.2 mol

Numerical Value Type

- What volume of 90% alcohol by weight ($d = 0.8 \text{ g mL}^{-1}$) must be used to prepare 80 mL of 10% alcohol by weight ($d = 0.9 \text{ g mL}^{-1}$)?
- 50 mL of 1 M HCl, 100 mL of 0.5 M HNO_3 , and x mL of 5 M H_2SO_4 are mixed together and the total volume is made up to 1.0 L with water. 100 mL of this solution exactly neutralises 10 mL of $M/3 \text{ Al}_2(\text{CO}_3)_3$. Calculate the value of x .
- How many mL of a solution of concentration 100 mg Co^{2+} per mL is needed to prepare 10 mL of a solution of concentration 20 mg Co^{2+} per mL.
- HCl gas is passed into water, yielding a solution of density 1.095 g mL^{-1} and containing 30% HCl by weight. Calculate the molarity of the solution.
- A solution contains 75 mg NaCl per mL. To what extent must it be diluted to give a solution of concentration 15 mg NaCl per mL of solution.
- To prepare 100 g of a 92% by weight solution of NaOH, how many g of H_2O is needed?
- A person takes 6.1 g of an anta-acid tablet comprising bicarbonate ion at 20.8%. The volume of CO_2 evolved at (1 atm and 25°C) in the stomach (on neutralisation) multiplied

- by a factor of '10' will be x L. Calculate the approximate (integer) value of x .
8. The specific gravity of a salt solution is 1.025. If V mL of water is added to 1.0 L of this solution to make its density 1.02 g mL^{-1} , what is value of V in mL approximately?
9. A 19.6 g of a given gaseous sample contains 2.8 g of

molecules ($d = 0.75 \text{ g L}^{-1}$), 11.2 g of molecules ($d = 3 \text{ g L}^{-1}$) and 5.6 g of molecules ($d = 1.5 \text{ g L}^{-1}$). All density measurements are made at STP. Calculate the total number of molecules (N) present in the given sample. Report your answer in ' $10^{23} N$ '.

Assume Avogadro's number as 6×10^{23} .

Archives

JEE MAIN

Single Correct Answer Type

- The mass of potassium dichromate crystals required to oxidize 750 cm^3 of 0.6 M Mohr's salt solution is (molar mass = 392)

(1) 0.49 g	(2) 0.45 g
(3) 22.05 g	(4) 2.2 g

 (AIEEE 2011)
- The molality of a urea solution in which 0.0100 g of urea, $[(\text{NH}_2)_2\text{CO}]$ is added to 0.3000 dm^3 of water at STP is

(1) $5.55 \times 10^{-4} \text{ M}$	(2) 33.3 M
(3) $3.33 \times 10^{-2} \text{ M}$	(4) 0.555 M

 (AIEEE 2011)
- The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL . The molarity of this solution is

(1) 0.50 M	(2) 1.78 M
(3) 1.02 M	(4) 2.05 M

 (AIEEE 2012)
- The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be

(1) 0.875 M	(2) 1.00 M
(3) 1.75 M	(4) 0.0975 M

 (JEE Main 2013)
- A gaseous hydrocarbon gives upon combustion, 0.72 g of water and 3.08 g of CO_2 . The empirical formula of the hydrocarbon is

(1) C_2H_4	(2) C_3H_4
(3) C_6H_5	(4) C_7H_8

 (JEE Main 2013)
- The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is $1:4$. The ratio of number of their molecule is

(1) $1:4$	(2) $1:8$
(3) $7:32$	(4) $3:16$

 (JEE Main 2014)
- At 300 K and 1 atm , 15 mL of a gaseous hydrocarbon requires 375 mL air containing $20\% \text{ O}_2$ by volume for complete combustion. After combustion the gases occupy 330 mL . Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is:

(1) C_4H_{10}	(2) C_3H_6
(3) C_3H_8	(4) C_4H_8

 (JEE Main 2016)

8. The most abundant elements by mass in the body of a healthy human adult are Oxygen (61.4%); Carbon (22.9%). Hydrogen (10.0%); and Nitrogen (2.6%). The weight which a 75 kg person would gain if all ^1H atoms are replaced by ^2H atoms is:

- | | |
|----------------------|-----------------------|
| (1) 15 kg | (2) 37.5 kg |
| (3) 7.5 kg | (4) 10 kg |

(JEE Main 2017)

9. 1 gram of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2 . The molar mass of M_2CO_3 in g mol^{-1} is:

- | | |
|-----------|-----------|
| (1) 1186 | (2) 84.3 |
| (3) 118.6 | (4) 11.86 |

(JEE Main 2017)

10. The ratio of mass percent of C and H of an organic compound ($\text{C}_x\text{H}_y\text{O}_z$) is $6:1$. If one molecule of the above compound ($\text{C}_x\text{H}_y\text{O}_z$) contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O . The empirical formula of compound $\text{C}_x\text{H}_y\text{O}_z$ is:

- | | |
|--------------------------------------|--------------------------------------|
| (1) $\text{C}_2\text{H}_4\text{O}$ | (2) $\text{C}_3\text{H}_4\text{O}_2$ |
| (3) $\text{C}_2\text{H}_4\text{O}_3$ | (4) $\text{C}_3\text{H}_6\text{O}_3$ |

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

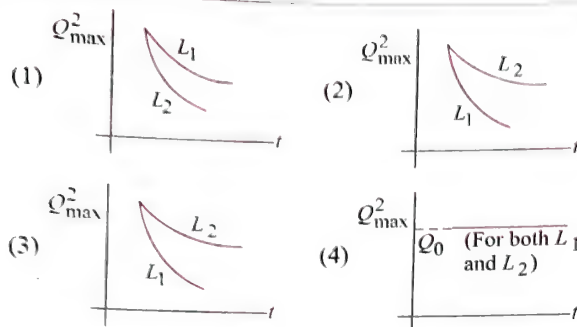
- Given that the abundance of isotopes ^{54}Fe , ^{56}Fe , and ^{57}Fe is 5% , 90% , and 5% , respectively. The atomic mass of Fe is

(1) 55.85	(2) 55.95
(3) 55.75	(4) 55.05

 (IIT-JEE 2009)
- Dissolving 120 g of urea ($M_w = 60$) in 1000 g of water gave a solution of density 1.15 g mL^{-1} . The molarity of solution is:

(1) 1.78 M	(2) 2.00 M
(3) 2.05 M	(4) 2.22 M

 (IIT-JEE 2011)
- If a student plots graphs of the square of maximum charge (Q_{max}^2) on the capacitor with time (t) for two different values L_1 and L_2 ($L_1 > L_2$) of L then which of the following represents this graph correctly? (Plots are schematic and not drawn to scale)



(JEE Advanced 2015)

4. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (Mol. wt. 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin?

- (1) $\frac{1}{103}$ (2) $\frac{1}{206}$ (3) $\frac{2}{309}$ (4) $\frac{1}{412}$

(JEE Advanced 2015)

Numerical Value Type

1. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is

(IIT-JEE 2010)

2. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is

(IIT-JEE 2010)

3. Silver (atomic weight 108 g mol^{-1}) has a density of 10.5 g cm^{-3} . The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^{-x}$. The value of x is

(IIT-JEE 2010)

4. Among the following, what is the number of elements showing only one non-zero oxidation state?

O, Cl, F, N, P, Sn, Tl, Na, Ti

(IIT-JEE 2010)

5. 29.2 (w/w) HCl stock solution has a density of 1.25 g mL^{-1} . The molecular weight of HCl is 36.5 g mol^{-1} . The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is

(IIT-JEE 2012)

6. If the value of Avogadro number is $6.023 \times 10^{23} \text{ mol}^{-1}$ and the value of Boltzmann constant is $1.380 \times 10^{-23} \text{ JK}^{-1}$, then the number of significant digits in the calculated value of the universal gas constant is

(JEE Advanced 2014)

7. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL^{-1} . Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is

(JEE Advanced 2014)

8. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3} . The ratio of the molecular weights of the solute and solvent

$$\left(\frac{MW_{\text{solute}}}{MW_{\text{solvent}}} \right), \text{ is}$$

(JEE Advanced 2016)

Answers Key**EXERCISES****Single Correct Answer Type**

- | | | | | |
|---------|---------|------------|---------|---------|
| 1. (2) | 2. (2) | 3. (3) | 4. (2) | 5. (1) |
| 6. (2) | 7. (1) | 8. (1) | 9. (2) | 10. (1) |
| 11. (1) | 12. (1) | 13. (4) | 14. (1) | 15. (3) |
| 16. (1) | 17. (1) | 18. (2, 1) | 19. (1) | 20. (1) |
| 21. (1) | 22. (2) | 23. (3) | 24. (2) | 25. (2) |
| 26. (1) | 27. (1) | 28. (4) | 29. (3) | 30. (2) |
| 31. (3) | 32. (2) | 33. (1) | 34. (2) | 35. (2) |
| 36. (2) | 37. (3) | 38. (3) | 39. (2) | 40. (3) |
| 41. (1) | 42. (3) | 43. (1) | 44. (4) | 45. (1) |
| 46. (4) | 47. (3) | 48. (2) | 49. (2) | 50. (3) |
| 51. (2) | 52. (4) | 53. (4) | 54. (1) | 55. (3) |
| 56. (4) | 57. (2) | 58. (1) | 59. (2) | 60. (3) |

Multiple Correct Answers Type

- | | | |
|------------------|------------------|------------------|
| 1. (1, 2) | 2. (2, 3) | 3. (4) |
| 4. (1, 2, 3, 4) | 5. (3, 4) | 6. (1, 4) |
| 7. (1, 2, 3, 4) | 8. (1, 2, 3, 4) | 9. (1, 2, 3) |
| 10. (1, 2, 3, 4) | 11. (1, 2, 3, 4) | 12. (2, 3, 4) |
| 13. (3, 4) | 14. (1, 2, 4) | 15. (1, 4) |
| 16. (2, 3) | 17. (2, 3, 4) | 18. (1, 2, 3) |
| 19. (1, 3) | 20. (1, 2, 3, 4) | 21. (1, 2, 3, 4) |
| 22. (3, 4) | 23. (3, 4) | 24. (1, 3, 4) |
| 25. (3, 4) | 26. (1, 2) | 27. (1, 2, 3, 4) |
| 28. (1, 3) | 29. (1, 2, 4) | 30. (1, 2, 3, 4) |
| 31. (1, 3, 4) | 32. (4, 2) | 33. (1, 4) |
| 34. (1, 2, 3) | 35. (1, 3) | 36. (3, 4) |

Linked Comprehension Type

1. (2) 2. (3) 3. (1) 4. (2) 5. (4)
 6. (2) 7. (4) 8. (1) 9. (2) 10. (4)
 11. (1) 12. (4)

Matrix Match Type

Q.No.	a	b	c	d
1.	q	r	s	p
2.	q	p	r	s
3.	p,q,r	q	q	p,q,r
4.	r	s	p	q
5.	p,q,r,t	q,r,t	p,q,r,s	r,t
6.	p,s	p,q,s	p,r	r
7.	p,q,r	p,q,r	q,s	s

Numerical Value Type

1. (10) 2. (10) 3. (2) 4. (9) 5. (5)
 6. (8) 7. (7) 8. (5) 9. (3)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (3) 2. (1) 3. (4) 4. (1) 5. (4)
 6. (3) 7. (3) 8. (1) 9. (2) 10. (3)

JEE Advanced**Single Correct Answer Type**

1. (2) 2. (3) 3. (1) 4. (4)

Numerical Value Type

1. (3) 2. (3) 3. (7) 4. (2) 5. (8)
 6. (4) 7. (8) 8. (9)

2

Redox Reaction

2.1 INTRODUCTION

Chemistry is essentially a study of oxidation–reduction or redox reactions which involve transfer of electrons either between the atoms of the same molecule or between the atoms of different molecules. Redox reactions can take place either in the gas phase or in solution or they may involve more than one phase (heterogeneous reactions) and occur both in inorganic and organic compounds.

Both physical and biological phenomena are concerned with redox reactions. These reactions are used in biological, pharmaceutical, industrial, agricultural, and metallurgical areas.

Some examples of redox reactions are as follows:

- Burning of different types of fuels, e.g., coal, wood, petrol, diesel, kerosene, LPG (liquefied petroleum gas), CNG (compressed natural gas), etc., for obtaining energy for transport, domestic, and other commercial purposes.
- Electrochemical processes for the manufacture of highly reactive metals and non-metals, e.g., manufacture of *chlorine and caustic soda (NaOH)*, *corrosion of metals*, and *operation of dry and wet batteries*.
- Development of *ozone hole* and environmental issues such as *hydrogen economy* (use of liquid hydrogen as fuel) are the latest examples of redox reactions.

2.2 OXIDATION

Oxidation is the process of addition of oxygen or any electronegative element or group or removal of hydrogen or any electropositive element or group. For example:

- $2\text{Mg(s)} + \text{O}_2\text{(g)} \xrightarrow{[\text{O}]} 2\text{MgO(s)}$ (Addition of oxygen)
- $2\text{FeCl}_2\text{(aq)} + \text{Cl}_2\text{(g)} \xrightarrow{[\text{O}]} 3\text{FeCl}_3\text{(aq)}$
(Addition of electronegative element)
- $\text{H}_2\text{S(g)} + \text{Cl}_2\text{(g)} \xrightarrow{[\text{O}]} 2\text{HCl(g)} + \text{S(s)}$
(Removal of hydrogen)
- $\text{K}_2\text{MnO}_4\text{(aq)} + \text{O}_3\text{(g)} + \text{H}_2\text{O(l)} \xrightarrow{[\text{O}]} \text{KMnO}_4\text{(aq)} + \text{KOH(aq)}$
(Removal of electropositive element)

2.3 REDUCTION

Reduction is the process of addition of hydrogen or any electropositive element or group or removal of oxygen or any electronegative element or group. For example:

- $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \xrightarrow{[\text{R}]} 2\text{HCl(g)}$ (Addition of hydrogen)
- $2\text{HgCl}_2\text{(aq)} + \text{SnCl}_2\text{(aq)} \xrightarrow{[\text{R}]} \text{Hg}_2\text{Cl}_2\text{(s)} + \text{SnCl}_4\text{(aq)}$
(Addition of electropositive element)
- $\text{ZnO(s)} + \text{C(s)} \xrightarrow{[\text{R}]} \text{Zn(s)} + \text{CO(g)}$
(Removal of oxygen)
- $2\text{FeCl}_3\text{(aq)} + \text{H}_2\text{S(g)} \xrightarrow{[\text{R}]} \text{FeCl}_2\text{(aq)} + 2\text{HCl(aq)} + \text{S(s)}$
(Removal of electronegative element)

2.4 ELECTRONIC CONCEPT OF OXIDATION AND REDUCTION

- Oxidation:** It is a process in which an atom or a group of atoms taking part in a chemical reaction loses one or more electrons. For example:
 - $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2e^-$
 - $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$
 - $\text{S}^{2-} \longrightarrow \text{S} + 2e^-$
 - $\text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^- + e^-$
- Reduction:** It is a process in which an atom or a group of atoms taking part in a chemical reaction gains one or more electrons. For example:
 - $\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$
 - $2\text{Hg}^{2+} + 2e^- \longrightarrow \text{Hg}_2^{2+}$
 - $\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$
 - $\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$

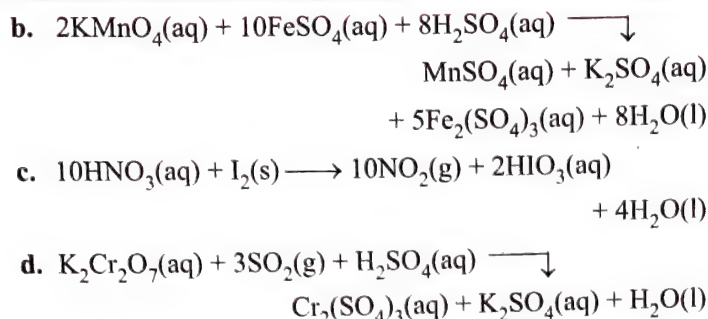
2.5 OXIDISING AGENT OR OXIDANT

An oxidising agent or oxidant is a substance which supplies oxygen or any other electronegative element or removes hydrogen or any other electropositive element. Alternatively, an oxidising agent or oxidant is that substance which itself undergoes reduction in a chemical reaction.

For example, O_2 , Cl_2 , and O_3 in reactions (a) to (d) given in Section 2.2 are oxidising agents.

Some examples of oxidising agents are MnO_2 (manganese dioxide), KMnO_4 (potassium permanganate), HNO_3 (nitric acid), and $\text{K}_2\text{Cr}_2\text{O}_7$ (potassium dichromate).

- $\text{MnO}_2\text{(s)} + 4\text{HCl(aq)} \longrightarrow \text{MnCl}_2\text{(aq)} + \text{Cl}_2\text{(g)} + 2\text{H}_2\text{O(l)}$

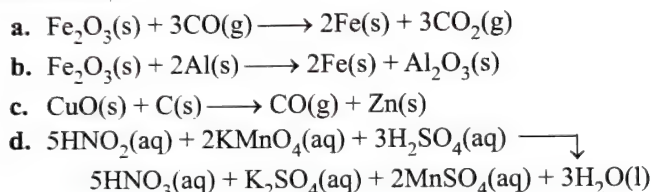


2.6 REDUCING AGENT OR REDUCTANT

A reducing agent or reductant is a substance which supplies hydrogen or any other electropositive element or removes oxygen or any other electronegative element. Alternatively, a reducing agent is that substance which itself undergoes oxidation in a chemical reaction.

For example, H_2 , SnCl_2 , C , and H_2S in reactions (a) to (d) given in Section 2.3 are reducing agents.

Some examples of reducing agents are CO , Al , C , and HNO_2 (nitrous acid).



2.7 OXIDATION NUMBER AND STATE

Oxidation number is defined as the residual charge which an atom of the element appears to have when all other atoms that form the molecule are removed as ions. Oxidation numbers are also called oxidation states.

Note: A redox reaction involves two half reactions: oxidation half reaction and reduction half reaction.

Now, a new concept of oxidation number and oxidation states is being introduced in order to study oxidation and reduction reactions (redox reactions) in a much better way.

Oxidation number: It refers to the total charge on all atoms of same kind in a compound.

Oxidation state: It refers to the charge per atom of all atoms of same kind in a compound.

Oxidation state, many a times, is also referred to as oxidation number.

This means the oxidation number of an element in a compound is equal to the oxidation state of that element multiplied by the total number of atoms of that element in that particular compound.

- a. In ionic compounds, it is simply the charge on the corresponding cation and anion expressed as the oxidation state of that particular element. For example, the oxidation states of potassium and chlorine in potassium chloride (KCl) are simply +1 and -1, respectively, as KCl is treated as K^+Cl^- .

Consider the following examples where oxidation states are written above the atoms:

+2-1	+2-2	+3-1	+2-2	+1-1	+1+6-2
MgCl_2	CaS	AlCl_3	CaO	NaF	K_2SO_4

Note: a. In MgCl_2 and AlCl_3 , -1 is the oxidation state of Cl atom and its oxidation numbers are -2 and -3, respectively.

b. In each of the above cases, the sum of oxidation number of all the atoms of all kinds is equal to zero (as the compound is neutral).

b. In covalent compounds, it is not so easy to assign oxidation state to an atom. In order to simplify the concept, we are going to define a set of rules which would enable us to assign oxidation state to every element in any compound.

2.7.1 RULES FOR ASSIGNING OXIDATION NUMBER AND STATE

- Any element in free state is assigned an oxidation state of zero (0). For example, the oxidation state of H , P , S , O , Fe , and Br in H_2 , P_4 , S_8 , O_2 , Fe , and Br_2 , respectively, is equal to 0.
- The oxidation state of any cation or anion (of form A^{\oplus} or B^{\ominus}) is equal to the magnitude of its charge. For example, the oxidation state of Ca in $\text{Ca}^{2+} = +2$, the oxidation state of Al in $\text{Al}^{3+} = +3$, the oxidation state of Cl in $\text{Cl}^- = -1$, and so on.
- The algebraic sum of the oxidation numbers of all atoms in a neutral compound is equal to 0.
 - The algebraic sum of the oxidation numbers of all atoms in an ion (such as PO_4^{3-}) is equal to the charge on the ion.
- The oxidation state of alkali metals (group IA) is +1 in all of their compounds and that of alkaline earth elements (group IIA) is +2 in all of their compounds.
- Hydrogen, in almost all of its compounds, is assigned an oxidation state of +1. The exception occurs when hydrogen forms compounds with strong metals (metallic hydrides). For example, KH , NaH , MgH_2 , CaH_2 , etc. In all of these, the oxidation state of hydrogen is -1.
- Oxygen, in almost all of its compounds, is assigned an oxidation state of -2. In a class of compounds called peroxides, the oxidation state of oxygen is -1. For example, H_2O_2 , Na_2O_2 , etc. Other exceptions are OF_2 where the oxidation state is +2, O_2F_2 where the oxidation state is +1, and KO_2 in which the oxidation state is -1/2.
- Fluorine is the most electronegative element and is assigned an oxidation state of -1 in all its compounds. For other halogens, oxidation state is generally -1 except when they are bonded to a more electronegative halogen or oxygen. Oxidation state of iodine in IF_7 is +7, oxidation state of chlorine in KClO_3 is +5.

ILLUSTRATION 2.1

Calculate the oxidation number of all the atoms in the following compounds and ions:

- a. PbSO_4 b. CrO_4^{2-} c. Sb_2O_5 d. $(\text{NH}_4)_2\text{SO}_4$

Sol. a. In PbSO_4 or $\text{Pb}^{2+}(\text{SO}_4)^{2-}$

Oxidation number of $\text{Pb} = +2$.

Oxidation number of each O atom = -2

Let oxidation number of S = x

$$\therefore +2 + x + 4(-2) = 0 \Rightarrow 2 + x - 8 = 0 \Rightarrow x = +6$$

Hence, oxidation number of S in PbSO_4 = +6

b. In CrO_4^{2-}

Oxidation number of each O atom = -2

Let oxidation number of Cr = x

$$x + 4(-2) = -2 \Rightarrow x - 8 = -2 \Rightarrow x = +6$$

Hence, oxidation number of Cr in CrO_4^{2-} = +6.

c. In Sb_2O_5

Oxidation number of each O atom = -2

Let oxidation number of Sb = x

$$2x + 5(-2) = 0 \Rightarrow 2x - 10 = 0 \Rightarrow x = +5$$

Hence, oxidation number of Sb in Sb_2O_5 = +5

d. In $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4^+)_2\text{SO}_4^{2-}$

Let oxidation number of N in NH_4^+ = x

Oxidation number of each H atom = +1

$$x + 4(+1) = +1 \text{ (taking } \text{NH}_4^+)$$

$$x = -3$$

Hence, oxidation number of N in $(\text{NH}_4)_2\text{SO}_4$ = -3

and oxidation number of each O atom = -2

Let oxidation number of S = x

$$\therefore x + 4(-2) + 2 \text{ (taking } \text{SO}_4^{2-})$$

$$x - 8 = -2 \Rightarrow \text{or } x = +6$$

Hence, oxidation number of S in $(\text{NH}_4)_2\text{SO}_4$ = 6

ILLUSTRATION 2.2

Determine the oxidation number of follo-wing underlined elements:

- | | |
|--|---|
| a. HCN | b. HNC |
| c. HNO_3 | d. KO_2 |
| e. Fe_3O_4 | f. KI_3 |
| g. N_3H | h. $\text{Fe}(\text{CO})_5$ |
| i. $\text{Fe}_{0.94}\text{O}$ | j. NH_2NH_2 |
| k. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | l. NOCl |
| m. NOClO_4 | n. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ |
| o. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$ | p. $\text{Na}_2\text{S}_4\text{O}_6$ |
| q. $(\text{CH}_3)_2\text{SO}$ | r. $\text{Na}_2\text{S}_2\text{O}_3$ |
| s. CaOCl_2 | |

Sol.

- a. **HCN**: The evaluation cannot be made directly in some cases, e.g., HCN, by using rules proposed earlier as we have no rule for the evaluation of the oxidation number of both N and C. In all such cases, evaluation of oxidation number should be made using indirect concept or using fundamentals by which following rules have been formed:

- Each covalently bond contributes one unit for oxidation number.
- Covalently bonded atoms with less electronegativity acquire positive oxidation number whereas other atoms with more electronegativity acquire negative oxidation number.
- In case of a coordinate bond, give +2 value for oxidation number to the atom from which coordinate bond is directed to a more electro-negative atom. If coordinate bond is directed from a more electronegative to a less electronegative atom, then neglect the contribution of coordinate bond for both atoms in which coordinate bond exists.

Thus, $\text{H}-\text{C}\equiv\text{N}$

Three bonds on N atom implies more electronegative

$$1 + a + 3(-1) = 0$$

$$\text{Oxidation number of N} = 3(-1) = -3$$

$$\text{Oxidation number of C, } a = +2$$

b. **HNC**: $\text{H}-\text{C}\equiv\text{N}$

$$\text{Oxidation number of H} = +1$$

$$\text{Oxidation number of N}$$

$$= [-2 + (-1) + 0] = -3$$

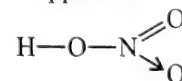
[For covalent bond with C] [For covalent bond with H] [No contribution for coordinate bond]

According to fundamental concept = -3

$$\therefore 1 + (-3) + a = 0 \Rightarrow a = +2$$

c. **HNO₃**: By rules, $1 + a + 3(-2) = 0 \Rightarrow a = +5$

By fundamental approach



$$\text{Oxidation number of H} = +1$$

$$\text{Oxidation number of N}$$

$$= +1 + (+2) + (+2) = +5$$

[Covalent bond with O] [Two covalent bonds with O; N being less electronegative than O] [Coordinate bond]

d. **KO₂**: A superoxide of K

$$\text{Oxidation number of K} = +1$$

$$\text{Oxidation number of O} = a$$

$$1 + 2(a) = 0 \text{ and } a = -1/2$$

e. **Fe₃O₄**: $3(a) + 4(-2) = 0 \Rightarrow a = +8/3$

Fe₃O₄ is a mixed oxide of FeO·Fe₂O₃.

Therefore, Fe has two oxidation numbers +2 and +3, respectively. However, factually speaking, oxidation number in Fe₃O₄ is an average of two values, i.e., +2 and +3.

$$\text{Therefore, average oxidation number} = \frac{+2 + (+3)}{3} = +\frac{8}{3}$$

f. KI_3 : $1 + 3(a) = 0 \Rightarrow a = -1/3$

Since KI_3 is $\text{KI} + \text{I}_2$, therefore, I has two oxidation numbers -1 and 0 , respectively.

However, oxidation number of I in KI_3 is an average of two values -1 and 0 .

Therefore, average oxidation number

$$= \frac{-1 + 2(0)}{3} = -\frac{1}{3}$$

g. N_3H : $3(a) + 1 = 0 \Rightarrow a = -1/3$

h. $\text{Fe}(\text{CO})_5$: Sum of oxidation number of $\text{CO} = 0$

$$\therefore a + 5(0) = 0 \Rightarrow a = 0$$

i. $\text{Fe}_{0.94}\text{O}$: $0.94(a) + (-2) = 0 \Rightarrow a = 200/94$

j. NH_2NH_2 : Both N have same nature, therefore each N has oxidation number -2 .

k. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$:

Oxidation number of $\text{Fe} = a$

Sum of oxidation number for $(\text{NH}_4)_2\text{SO}_4 = 0$

Sum of oxidation number of $\text{H}_2\text{O} = 0$

Sum of oxidation number of $\text{SO}_4^{2-} = -2$

$$\therefore a + (-2) + 0 + 6(0) = 0 \Rightarrow a = +2$$

l. NOCl : $\text{Cl}-\text{N}=\text{O}$ or use NO^+Cl^-

Oxidation number of $\text{N} = +1$ (for covalent bond with Cl)

Oxidation number of $\text{N} = +2$ (for two covalent bonds with O)

Therefore, oxidation number of N in $\text{NOCl} = +3$

m. NOClO_4 : The compound may be written as $\text{NO}^+\text{ClO}_4^-$ for ClO_4^- .

For ClO_4^- , let the oxidation number of $\text{Cl} = a$.

$$\therefore a + 4(-2) = -1 \Rightarrow a = +7$$

n. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$: NO in iron complex has NO^+ nature

$$\therefore 2 \times 1 + [a + 5(-1) + (+1)] = 0$$

$$\therefore a = +2$$

o. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$:

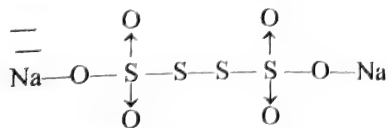
$$a + 1 + 5 \times 0 + (-2) = 0$$

$$\Rightarrow a = +1$$

p. $\text{Na}_2\text{S}_4\text{O}_6$: $2(+1) + 4a + 6(-2) = 0$

$$\therefore a = +5/2$$

Here also, this value is the average oxidation number of S. The structure of $\text{Na}_2\text{S}_4\text{O}_6$ is



Thus, oxidation number of each S atom forming coordinate bond is $+5$, whereas oxidation number of each S atom involved in pure covalent bonding is zero. Therefore, average oxidation number

$$= \frac{+5 + 5 + 0 + 0}{4} = +\frac{5}{2}$$

q. Dimethyl sulphoxide or $(\text{CH}_3)_2\text{SO}$:

Oxidation number of $\text{CH}_3 = +1$

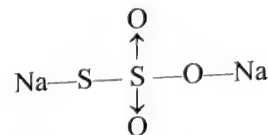
Oxidation number of $\text{O} = -2$

$$\therefore 2(+1) + a + (-2) = 0 \Rightarrow a = 0$$

r. $\text{Na}_2\text{S}_2\text{O}_3$: $2 \times 1 + 2 \times a + 3(-2) = 0 \Rightarrow a = +2$

Here too, it is the average oxidation number.

The structure of $\text{Na}_2\text{S}_2\text{O}_3$ is



The oxidation number of S involved in coordinate bond, i.e., donor S atom, is $+5$. The oxidation number of other S atom is -1 .

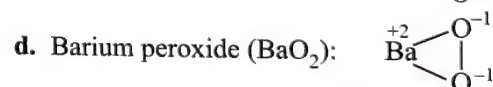
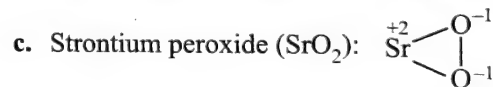
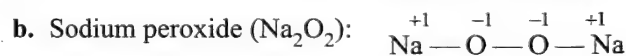
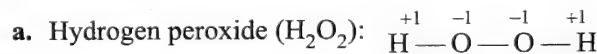
s. CaOCl_2 : In bleaching powder, two Cl atoms are as $\text{Ca}(\text{OCl})\text{Cl}$, i.e., one as Cl^- having oxidation number -1 and other as OCl^- having oxidation number $+1$.

2.8 OXIDATION STATE OF OXYGEN IN DIFFERENT FORMS

2.8.1 OXIDATION STATE OF OXYGEN IN PEROXIDES AND PERACIDES

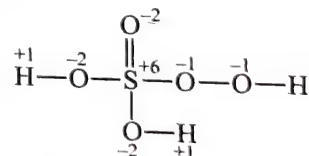
Oxidation state (oxidation number) of oxygen in peroxides ($-\text{O}-\text{O}-$), e.g., H_2O_2 , and peroxyacids is -1 .

For example:



e. Peroxosulphuric acid or peroxy sulphuric acid or permono oxosulphuric acid or persulphuric acid or Caro's acid (H_2SO_5):

Structure:



i. Calculation of oxidation state of S in H_2SO_5 and their anions:

Two oxygen in peroxide bond are in -1 oxidation state
 $= -1 \times 2 = -2$

Three oxygen in -2 oxidation state $= -2 \times 3 = -6$

$$\therefore \text{H}_2\text{SO}_5 = 2 + x - 2 - 6 = 0 \Rightarrow x = 6$$

Oxidation number of S $= +6$

ii. HSO_5^- (monohydroperoxy sulphate ion):

$$\text{HSO}_5^- = 1 + x - 2 - 6 = -1 \Rightarrow x = 6$$

Oxidation number of S $= 6$

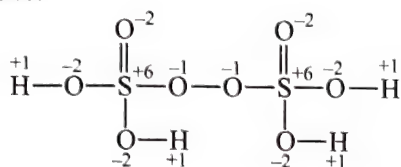
iii. SO_5^{2-} (peroxosulphate ion)

$$\text{SO}_5^{2-} = x - 2 - 6 = -2 \Rightarrow x = 6$$

Oxidation number of S = +6

f. Peroxodisulphuric acid or peroxydisulphuric acid or permonooxodisulphuric acid or per disulphuric acid or Marshall's acid ($\text{H}_2\text{S}_2\text{O}_8$):

Structure:

i. Oxidation state and oxidation number of S in $\text{H}_2\text{S}_2\text{O}_8$ and their anions:Two oxygen in peroxide bond are in -1 oxidation state
 $= -1 \times 2 = -2$ Six oxygen in $\text{H}_2\text{S}_2\text{O}_8$ are in -2 oxidation state
 $= -2 \times 6 = -12$

$$\therefore \text{H}_2\text{S}_2\text{O}_8 : \quad 2 + 2x - 2 - 12 = 0 \\ 2x = 12 \Rightarrow x = 6$$

Oxidation number of S in $\text{H}_2\text{S}_2\text{O}_8 = +6$.ii. Monohydroperoxodisulphate ion or hydro-persulphate ion ($\text{HS}_2\text{O}_8^{\ominus}$):

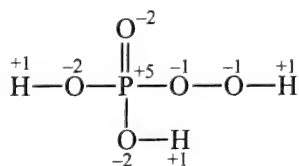
$$1 + 2x - 2 - 12 = -1 \\ 2x = 12 \Rightarrow x = 6$$

Oxidation number of S in $\text{HS}_2\text{O}_8^{\ominus} = 6$ iii. Peroxodisulphate ion or persulphate ion ($\text{S}_2\text{O}_8^{2-}$):

$$2x - 2 - 12 = -2 \\ 2x = 12 \Rightarrow x = 6$$

Oxidation number of S in $\text{S}_2\text{O}_8^{2-} = +6$ g. Peroxophosphoric acid or peroxyphosphoric acid or permonooxophosphoric acid or perphosphoric acid (H_3PO_5):

Structure:

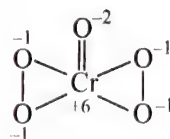
h. Oxidation state (oxidation number) of P in H_3PO_5 and their anions:Two oxygen in peroxide bond are in -1 oxidation state
 $= -1 \times 2 = -2$ Three oxygen in H_3PO_5 are in -2 oxidation state
 $= -2 \times 3 = -6$

$$\text{H}_3\text{PO}_5 = 3 + x - 2 - 6 = 0 \Rightarrow x = 5$$

Oxidation number of P = +5

Similarly, oxidation state of P in $\text{H}_2\text{PO}_5^{\ominus}$, HPO_5^{2-} , and PO_5^{3-} is +5.Likewise, oxidation state of C in H_2CO_4 (peroxocarbonic acid), HCO_4^{\ominus} , and CO_4^{2-} is +4.

Therefore, it is concluded from the above examples that oxidation state or oxidation number of an element in acids and its corresponding peracids remains same.

i. Chromium pentoxide (butterfly structure) (CrO_5):Oxidation state (oxidation number) of Cr in CrO_5 :There are two peroxide ($-\text{O}-\text{O}-$) bonds in CrO_5 .Four oxygen in two peroxide bond are in -1 oxidation state
 $= -1 \times 4 = -4$ One oxygen in CrO_5 is in -2 oxidation state
 $= -2 \times 1 = -2$

$$\therefore \text{CrO}_5 = x - 4 - 2 = 0 \Rightarrow x = +6$$

Oxidation number of Cr = +6

2.8.2 OXIDATION STATE OF OXYGEN IN SUPEROXIDES

Oxidation number of oxygen in superoxides is $-1/2$, e.g., in
 $\text{K}^{\overset{+2}{\text{O}}}_2$ (potassium superoxides) and $\text{Rb}^{\overset{+1}{\text{O}}}_2$ (rubidium superoxide).

2.8.3 OXIDATION STATE OF OXYGEN, WHEN IT IS BONDED TO FLUORINE

In such compounds, e.g., oxygen difluoride ($\text{O}^{\overset{+2}{\text{F}}}_2$) and dioxygen difluoride ($\text{O}_2^{\overset{+1}{\text{F}}}_2$), the oxygen is assigned an oxidation number of +2 and +1, respectively. The number assigned to oxygen depends upon the bonding state of oxygen but this number should be a positive figure only.

2.9 HIGHEST OXIDATION NUMBER STATE OF THE GROUP ELEMENT

It represents the group in which the element is present. For example, the highest oxidation number state of the element K in KCl is +1, since K is a first group element. Similarly, for the elements of other group, it is shown as below:

Group	1	2	13	14	15	16	17
Element	Cs	Ca	Al	Si	N	S	Br
Compound	CsBr	CaSO_4	AlF_3	SiBr_4	N_2O_5	SF_6	HBrO_4
Highest oxidation number state of the group element	+1	+2	+3	+4	+5	+6	+7

2.10 STOCK NOTATION

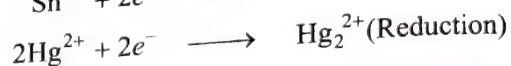
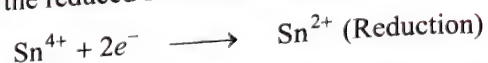
Oxidation state is often used interchangeably with oxidation number. Thus, the oxidation state and the oxidation number of C in CO_2 is +4, and the oxidation state and the oxidation number of O in CO_2 is -2. Thus, the oxidation number denotes the oxidation state of an element in a compound.The oxidation number state of a metal in a compound is sometimes represented by *Stock notation* given by German chemist Alfred Stock. In this notation, the oxidation number is expressed by a roman numeral such as I, II, III, IV, V, VI, VII, etc., indicating the oxidation state of the metal within parenthesis after the symbol or name of the metal.For example, nitrogen forms five oxides, i.e., N_2O , NO, NO_2 , N_2O_4 , and N_2O_5 having the oxidation number +1, +2, +4, +4, and

+5, respectively. Therefore, according to stock notation, they are represented as $N_2(I)O$, $N(II)O$, $N(IV)O_2$, $N_2(IV)O_4$, and $N_2(V)O_5$, respectively.

Similarly, aurous chloride and auric chloride are written as $Au(I)Cl$ and $Au(III)Cl_3$. Similarly, stannous chloride and stannic chloride are written as $Sn(II)Cl_2$ and $Sn(IV)Cl_4$, respectively. This change in oxidation state explains whether the species is present in oxidised or reduced form.

Thus, $Sn(II)Cl_2$ is the reduced form of $Sn(IV)Cl_4$. Similarly,

$Hg_2(I)Cl_2$ is the reduced form of $Hg(II)Cl_2$.



Note: Hg_2Cl_2 is also called calomel and is an ionic compound, while $HgCl_2$ is also called corrosive sublimate and is a covalent compound and poisonous, antidote of this is white of an egg.

Table 2.1 Difference between valency and oxidation number (these two terms have different meanings as explained below)

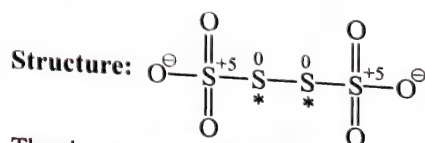
Oxidation number		Valency	
1.	Oxidation number is the residual charge left on the atom when other atoms are removed as ions.	1.	It is the combining capacity of an element. It is also defined as the number of H atoms or twice the number of O atoms with which an atom of the element reacts.
2.	It can be zero, e.g., oxidation number of C in CH_2Br_2 is zero.	2.	It cannot be zero.
3.	It refers to the charge, which can be positive or negative, e.g., in $CuCl_2$, the oxidation number of Cu is +2 and that of Cl is -1.	3.	It is only a number and it is not assigned as positive or negative. For example, in $CuCl_2$, the valency of Cu is 2 and that of Cl is 1.
4.	It can have fractional value, e.g., oxidation number of S in $K_2S_2O_8$ is +5/2.	4.	It is always a whole number, since atoms always combine in simple whole numbers.
5.	Oxidation number of an element can be different in different compounds, e.g., oxidation number of C in CH_4 , C_2H_6 , CH_3Br , C_2H_2 , CH_2Br_2 , CCl_4 , and $CHBr_3$ are -4, -3, -2, -1, 0, +4, and +2, respectively.	5.	It is fixed in all its compounds, e.g., the valency of C is 4 in all its compounds, such as CH_4 , C_2H_6 , CH_3Br , C_2H_2 , CH_2Br_2 , CCl_4 , and $CHBr_3$.
6.	Oxidation number of an element can be variable but the variation is very large, e.g., oxidation number of N in N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , N_2 , N_2H_2 , N_2H_4 and NH_3 is +1, +2, +3, +4, +5, 0, -1, -2, and -3, respectively.	6.	For an element, it can be variable but is limited to only two values, e.g., the valency of N is either 3 or 4 in all its compounds, such as N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , $(N_2O) \Rightarrow :N \equiv N: \rightarrow O$ (or) $:\ddot{N}::\ddot{N}::\ddot{O}:$ (3 valency of each N) 2 valency 4 valency $(NO_2) \Rightarrow O \leftarrow :N=O$ (or) $\overset{\ominus}{O}-\overset{\oplus}{N}=O$ $(N_2O_3) \Rightarrow O=N-N \rightarrow O$ (or) $O=N-\overset{\oplus}{N}-\overset{\ominus}{O}$ 3 valency 4 valency $(N_2O_4) \Rightarrow O=N-N=O$ (or) $O=\overset{\oplus}{N}-\overset{\oplus}{N}=O$ (Four valency of each N) $(N_2O_5) \Rightarrow O=N-O-N=O$ (or) $O=\overset{\oplus}{N}-O-\overset{\oplus}{N}=O$ (Four valency of each N)

2.11 FRACTIONAL OXIDATION STATE

Fractional oxidation state is the average oxidation state of the element and the structural parameters show that the element whose oxidation state is determined is present in different oxidation state. Structures and oxidation numbers of the species $S_4O_6^{2-}$ (tetrathionate ion), C_3O_2 (carbon suboxide), and Br_3O_8 (tribromooctaoxide) show the following bonding situations:

a. $S_4O_6^{2-}$ ($4x - 12 = -2$, $x = 2.5$)

Oxidation number of S = 2.5



The element marked with asterisk in each species is showing different oxidation state (oxidation number) from the rest of the atoms of the same element in each of the species.

In the species $S_4O_6^{2-}$, each of the two extreme S atoms shows oxidation state of +5 and the middle S atom as 0. The average of oxidation numbers of the four sulphur atoms is 2.5, whereas the reality being +5, 0, 0, and +5 oxidation number, respectively, for each sulphur.

b. C_3O_2 ($3x - 4 = 0$, $x = 4/3$)

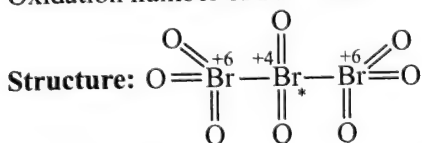
Oxidation number of C = $4/3$

Structure: $O \equiv C \equiv C \equiv C \equiv O$

In C_3O_2 , two terminal carbon atoms are present in +2 oxidation state each, whereas the third C atom (middle carbon) is in zero oxidation state and the average is $4/3$.

Br_3O_8 ($3x - 16 = 0$, $x = 16/3$).

Oxidation number of Br = $16/3$



In Br_3O_8 , each of the two terminal Br atoms is present in +6 oxidation state and the middle Br atom is present in +4 oxidation state. The average that is different from reality is $16/3$.

Therefore, in general, the fractional oxidation state reality is revealed by the structures only. It is concluded that fractional oxidation state is the average oxidation number only. This proves that the element in that particular species is present in more than one whole number oxidation states.

For example, Mn_3O_4 , Pb_3O_4 , and Fe_3O_4 are mixed oxides of ($2MnO + MnO_2$), ($2PbO + PbO_2$), and ($FeO + Fe_2O_3$), respectively, in which each metal atom shows fractional oxidation state. Likewise, oxidation state of oxygen in O_2^+ (dioxygenyl ion) and O_2^- (superoxide ion) is $+1/2$ and $-1/2$, respectively.

ILLUSTRATION 2.3

Using stock notation, represent the following compounds:

- | | | |
|--------------|------------|----------|
| a. $HAuCl_4$ | b. Tl_2O | c. FeO |
| d. Fe_2O_3 | e. CuI | f. CuO |
| g. MnO | h. MnO_2 | |

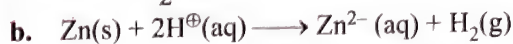
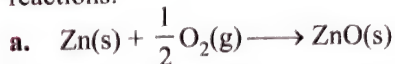
Sol.

	Compound	Stock notation	Name of the compound
a.	$^{+1}Au^{+3}Cl_4^{-1 \times 4}$ $HAuCl_4$	$HAu(III)Cl_4$	Hydroauric chloride
b.	$^{+1 \times 2}Tl_2^{+2}O^{-2}$ Tl_2O	$Tl_2(I)O$	Thallous oxide
c.	$^{+2}Fe^{+2}O^{-2}$ FeO	$Fe(II)O$	Ferrous oxide
d.	$^{+3 \times 2}Fe_2^{+6}O_3^{-2 \times 3}$ Fe_2O_3	$Fe_2(III)O_3$	Ferric oxide
e.	$^{+1}Cu^{+1}I^{-1}$ CuI	$Cu(I)I$	Cuprous iodide
f.	$^{+2}Cu^{+2}O^{-2}$ CuO	$Cu(II)O$	Cupric oxide
g.	$^{+2}Mn^{+2}O^{-2}$ MnO	$Mn(II)O$	Manganese oxide
h.	$^{+4}Mn^{+4}O_2^{-2 \times 2}$ MnO_2	$Mn(IV)O_2$	Manganese dioxide

CONCEPT APPLICATION EXERCISE 2.1

Subjective Type

1. Identify the oxidant and the reductant in the following reactions:



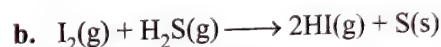
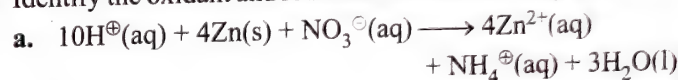
2. Find the oxidation number of sulphur in the following compounds: H_2S , H_2SO_4 , $S_2O_4^{2-}$, $S_2O_8^{2-}$, HSO_3^- .

3. Find the oxidation number of Cl in HCl , $HClO$, ClO_4^- , and $Ca(OCl)Cl$.

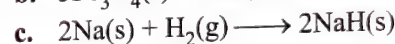
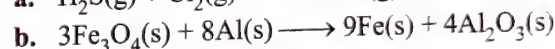
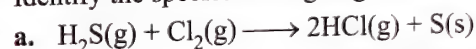
4. Find the oxidation number of carbon in the following compounds: CH_3OH , CH_2O , $HCOOH$, C_2H_2 .

5. Find the oxidation number of Fe in Fe_3O_4 and $Fe(III)_4[Fe(II)(CN)_6]_3$.

6. Identify the oxidant and reductant in the following reactions:

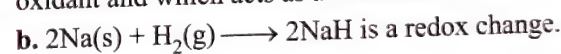


7. Identify the species undergoing oxidation and reduction.



8. a. Justify that the reaction

$2Cu_2O(s) + Cu_2S(s) \longrightarrow 6Cu(s) + SO_2(g)$ is a redox reaction. Identify the species oxidised/reduced. Which acts as an oxidant and which acts as a reductant?



9. Which of the following represents oxidation?

- | | |
|---------------------------------|--|
| a. $NO_2^- \longrightarrow N_2$ | b. $VO_2^- \longrightarrow VO_3^-$ |
| c. $ClO^- \longrightarrow Cl^-$ | d. $CrO_4^{2-} \longrightarrow Cr_2O_7^{2-}$ |

10. Using stock notation, represent the following compounds and write their names also.

- | | | | |
|------------------|--------------|-------------------|---------------|
| a. $Na_2Cr_2O_7$ | b. Mn_2O_7 | c. V_2O_5 | d. K_2CrO_4 |
| e. Cr_2O_3 | f. $FeSO_4$ | g. $Fe_2(SO_4)_3$ | h. $CuBr_2$ |
| i. Cu_2Br_2 | | | |

ANSWERS

Subjective Type

1. a. Zn(reductant), O(oxidant) b. Zn(reductant), H(oxidant)

2. H_2S : -2; H_2SO_4 : +6; $S_2O_4^{2-}$: +3; $S_2O_8^{2-}$: +6; HSO_3^- : +4

3. HCl : -1, $HClO$: +1; ClO_4^- : +7; $Ca(OCl)Cl$: 0

4. CH_3OH : -2; CH_2O : 0; $HCOOH$: +2; C_2H_2 : -1

5. Fe_3O_4 : $8/3$; $Fe(III)_4[Fe(II)(CN)_6]_3$: $18/7$

6. a. Zn(reductant), N(oxidant) b. S(reductant), I(oxidant)

7. Refer solutions.

8. a. S(reductant); Cu^+ (oxidant)

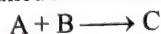
b. Yes, Na is oxidised and H_2 is reduced

9. c. 10. Refer to solutions.

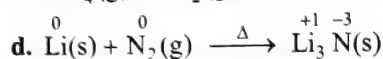
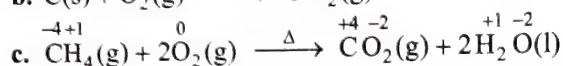
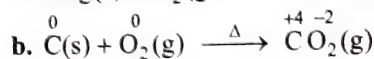
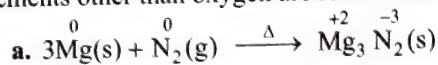
2.12 TYPES OF REDOX REACTIONS

2.12.1 COMBINATION REACTIONS

A reaction in which two atoms or molecules combine together to form a third molecule is called a combination reaction. For example:



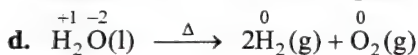
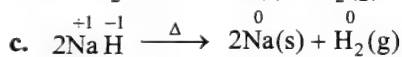
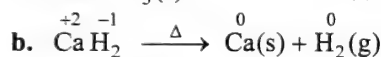
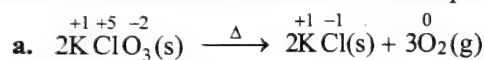
Either A or B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions in which elemental oxygen is used and all other reactions that involve elements other than oxygen are redox reactions. For example:



In reaction (c), there is no change in the oxidation number of hydrogen.

2.12.2 DECOMPOSITION REACTIONS

Decomposition reactions are those in which when a molecule breaks down to form two or more components, at least one of them must be in the elemental state. Thus, decomposition reactions are reverse of combination reactions. For example:



2.12.3 DISPLACEMENT REACTIONS

A reaction in which an atom or ion in a compound is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as:



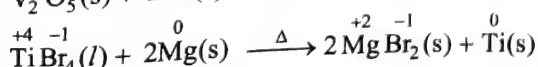
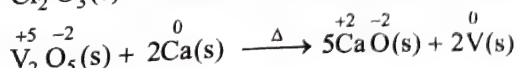
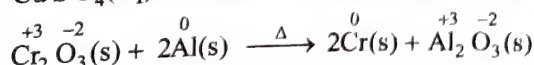
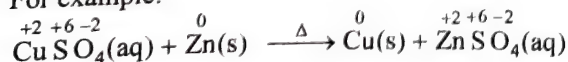
TYPES OF DISPLACEMENT REACTIONS

These are of two types:

- Metal displacement reactions
- Nonmetal displacement reactions

a. Metal displacement reactions: In these reactions, a metal in the compound is displaced by some other metal in the uncombined or elemental state. These reactions are used in metallurgical processes in which pure metals are obtained from their compounds in ores.

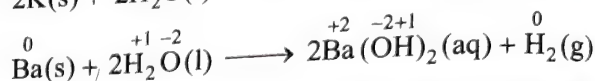
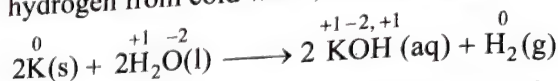
For example:



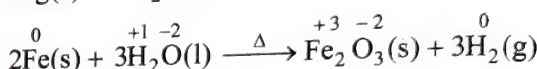
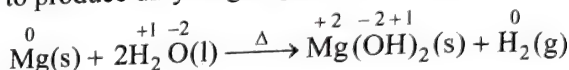
In all the above cases, the reducing metal is a better reducing agent than the one that is being reduced, which shows more capability to lose electrons as compared to the one that is reduced.

b. Nonmetal displacement reactions: In these reactions, a metal or nonmetal displaces another nonmetal from its compound. These nonmetal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen or halogens displacement.

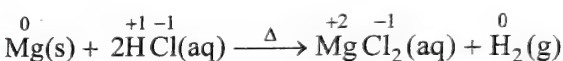
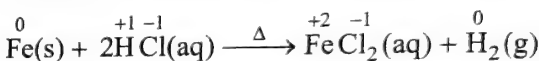
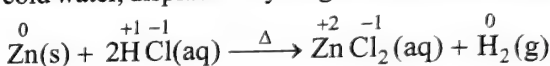
- All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants displace hydrogen from cold water, for example,



- Less reactive metals such as Mg and Fe react with steam to produce dihydrogen gas, for example,

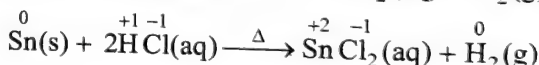
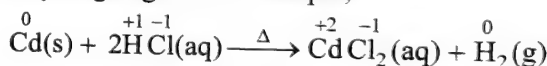


- Many metals, including those which do not react with cold water, displace dihydrogen from acids, for example,



The reactions of Zn and Mg with HCl are used in the preparation of dihydrogen gas in the laboratory.

- Metals such as Cd (cadmium) and Sn (tin) which do not react with steam but react with acids to produce dihydrogen gas. For example,



- Very less reactive metals such as silver (Ag) and gold (Au) which may occur in the native state do not react even with HCl.

Reactivity of Metals

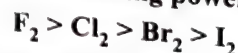
The reactivity of metals is determined by the rate of evolution of H_2 by metals from H_2O and aqueous acids, for example, Na reacts with water at the fastest rate, Mg reacts slowly, Fe reacts at the slowest rate while Ag, and Au do not react at all.

Order of reducing activity: $\text{Zn} > \text{Cu} > \text{Ag}$

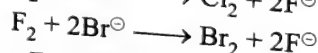
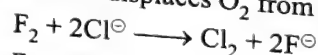
Reactivity of Nonmetals

The nonmetals, such as halogens, have a tendency to accept electrons, therefore, their reactivity depends upon their oxidising power.

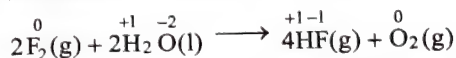
The order of decreasing oxidising power of halogens is:



Thus, F_2 is the strongest oxidising agent; it displaces Cl_2 , Br_2 , and I_2 from the solutions of their respective ions (Cl^- , Br^- , and I^-). F_2 is very reactive so it displaces O_2 from H_2O , for example,



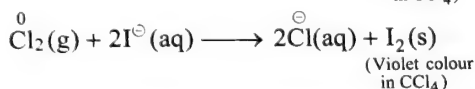
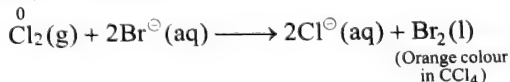
Reverse reactions in the above cases are not feasible.



Similarly, Cl_2 can displace Br^\ominus and I^\ominus ions and Br_2 can displace I^\ominus (but reverse reactions are not feasible).

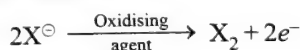
That is why displacement reactions of Cl_2 , Br_2 , and I_2 using F_2 are generally not carried out in aqueous solutions.

Layer Test: Chlorine can displace Br^\ominus and I^\ominus ions in an aqueous solution. As Br_2 and I_2 are brown and violet coloured and dissolve in CCl_4 , they can easily be identified from the colour of the solution, for example,



The above two reactions form the basis of identifying Br^\ominus and I^\ominus ions in the laboratory through the test known as **layer test**.

The halogen displacement reactions are used in industry for the recovery of halogens from their halides using suitable chemical oxidising agents.



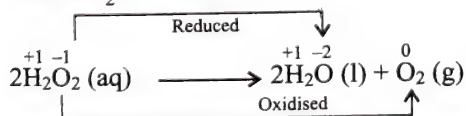
Oxidising agents such as KMnO_4 , MnO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc., are also used to oxidise Cl^\ominus , Br^\ominus , and I^\ominus ions to form Cl_2 , Br_2 , and I_2 , respectively. But no oxidising agent is available to oxidise F^\ominus ions to F_2 , since F_2 itself is the strongest oxidising agent. However, F_2 can be prepared by oxidising F^\ominus ions electrolytically.

2.12.4 DISPROPORTIONATION REACTIONS

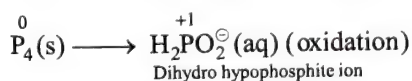
In a disproportionation reaction, an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state, and both lower and higher oxidation states of that element are formed in the reaction.

For example:

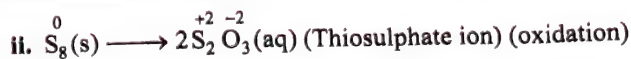
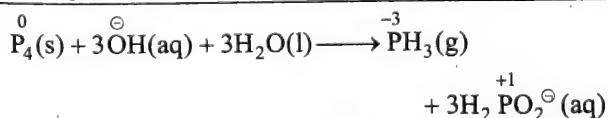
- a. Decomposition of H_2O_2 (hydrogen peroxide) to H_2O and O_2 . In H_2O_2 , -1 oxidation state of O is converted to zero oxidation state in O_2 and decreases to -2 oxidation state in H_2O .



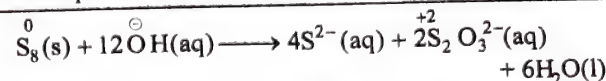
- b. Phosphorous, sulphur, and chlorine undergo disproportionation in the basic medium as given below:



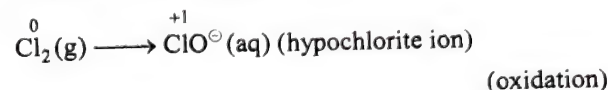
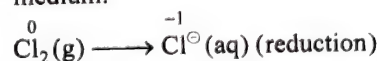
Net equation:



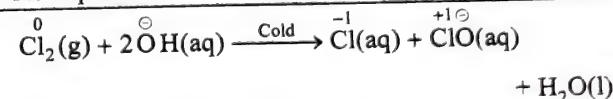
Net equation:



- iii. Reaction of Cl_2 , Br_2 , and I_2 in cold and dilute alkaline medium:



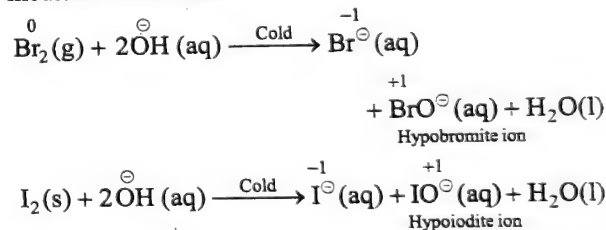
Net equation:



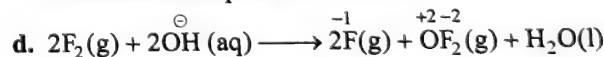
The reaction is the basis of household bleaching agent. The ClO^\ominus ion formed in the above reaction oxidises the colour-bearing stains of the substances to colourless compounds:

Bromine and iodine show the same trends as shown by chlorine in reaction (iii) above.

Similarly, the reaction of Br_2 and I_2 in cold alkaline medium is as follows:

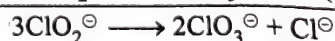
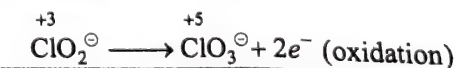
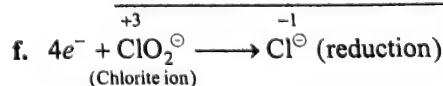
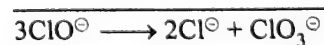
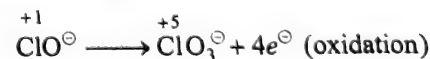
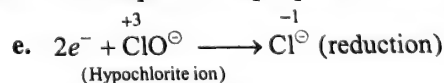


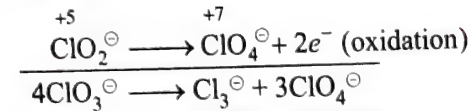
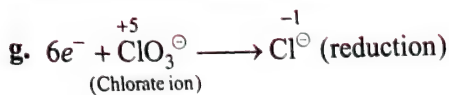
Fluorine does not show a disproportionation reaction since it is the most electronegative element, therefore it cannot exhibit any positive oxidation state. The reaction of fluorine takes place as follows:



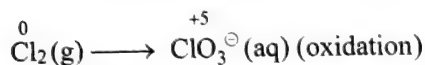
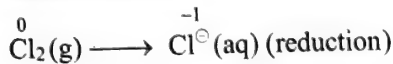
F_2 in reaction (d) will react with H_2O to produce some oxygen also.

Some more examples of disproportionation reactions:

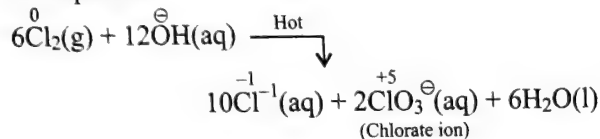




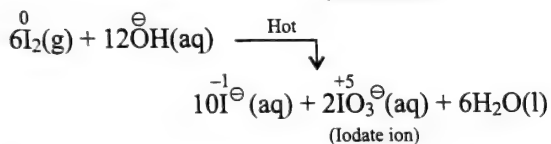
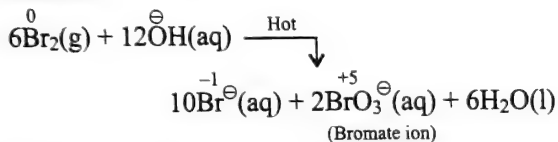
h. Reactions of Cl_2 , Br_2 , or I_2 in hot and concentrated alkaline medium.



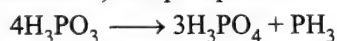
Net equation:



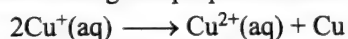
Similarly the reaction of Br_2 and I_2 in hot alkaline medium.



i. Ortho phosphorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

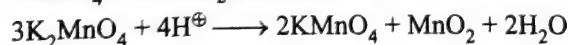


j. Many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

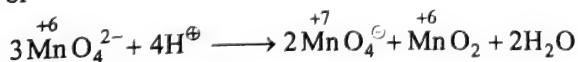


The higher stability of $\text{Cu}^{2+}(\text{aq})$ than $\text{Cu}^{+}(\text{aq})$ is due to the much more negative $\Delta_{\text{hyd}}\text{H}^{\ominus}$ of $\text{Cu}^{2+}(\text{aq})$ than that of Cu^{+} , which compensates the second ionisation enthalpy of Cu.

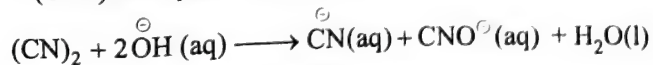
k. The dark green K_2MnO_4 (potassium manganate) disproportionates in a neutral or acidic solution to give KMnO_4 and MnO_2 (manganese dioxide).



or



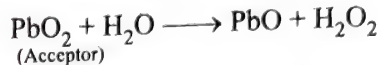
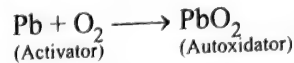
1. CN_2 (cyanogen), a colourless poisonous gas, disproportionates in basic solution to give cyanide (CN^-) and cyanate (CNO^-) ions.



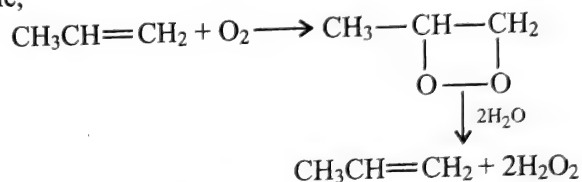
AUTOXIDATION OR INDUCED OXIDATION

Phosphorous and certain metals such as Zn and Pb and turpentine and numerous other unsaturated compounds can absorb oxygen from the air in presence of H_2O , which is oxidised to H_2O_2 . This

phenomenon of formation of H_2O_2 by the oxidation of H_2O is known as *autoxidation*. The substance (e.g., P, Zn, or turpentine) which activates the O_2 is called *activator*. The activator first combines with O_2 to form an addition compound, which acts as an *autoxidator* and reacts with H_2O or some other acceptor so as to oxidise the latter. For example,

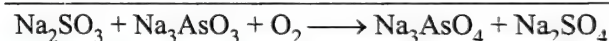


The unsaturated compounds which act as activators take up O_2 molecule at the double bond to form unstable peroxide which then gives up the O_2 to H_2O molecule or any other acceptor. For example,



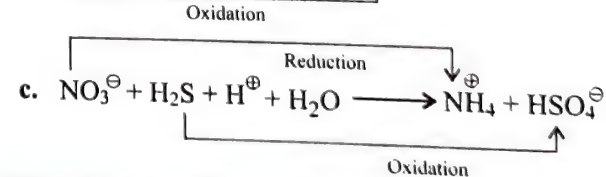
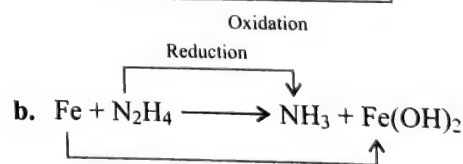
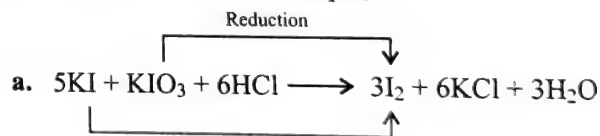
The evolved H_2O_2 is reacted with KI solution which gives I_2 . The evolution of I_2 from KI solution in presence of turpentine can be confirmed with starch solution which turns blue.

The phenomenon of induced oxidation can also be explained. Na_2SO_3 solution is oxidised by air but Na_3AsO_3 is not oxidised by air. If mixture of both is taken, then both are oxidised by air. This is called induced oxidation.



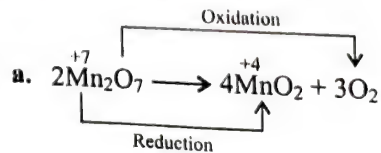
INTERMOLECULAR REDOX

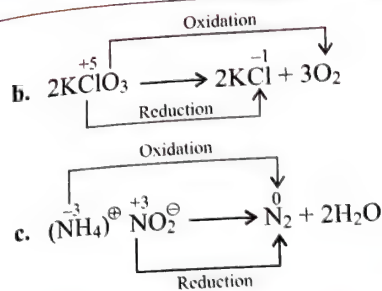
It is similar to redox in which one molecule is oxidised and other molecule is reduced. For example,



INTRAMOLECULAR REDOX

In this reaction one atom of a molecule is oxidised and another is reduced. For example,

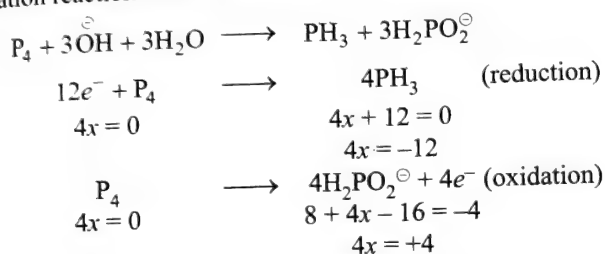




EQUIVALENT WEIGHT OF THE ELEMENT OR COMPOUND IN DISPROPORTIONATION REACTION

Equivalent weight is the sum of the equivalent weights in oxidation and reduction reaction, i.e., $(M/n_1 + M/n_2)$, where M is the molecular mass of the compound and n_1 and n_2 are the number of electrons in oxidation and reduction reactions, respectively.

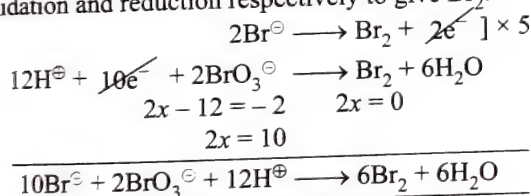
For example, the equivalent weight of P_4 in the disproportionation reaction shown below is:



$$E_w = \left(\frac{M}{4} + \frac{M}{12} \right) = \left(\frac{31 \times 4}{4} + \frac{31 \times 4}{12} \right) = \left(31 + \frac{31}{3} \right) = 38.75$$

CONPROPORTIONATION REACTION

Conproportionation reaction is the reverse of disproportionation reaction. For example, Br^- and BrO_3^- in acidic medium undergoes oxidation and reduction respectively to give Br_2 .



or



ILLUSTRATION 2.4

Which of the following species do not show disproportionation reaction and why?

BrO^- (hypobromite ion), BrO_2^- (bromite ion), BrO_3^- (bromate ion), and BrO_4^- (perbromate ion)

Sol. BrO_4^- does not disproportionate because in this oxoanion, Br is present in its highest oxidation state, i.e., +7. The disproportionation for other three oxoanions of Br is as follows:

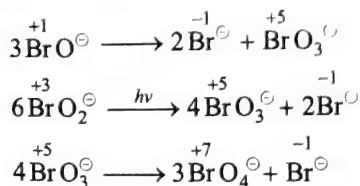


ILLUSTRATION 2.5

Classify the following redox reactions:

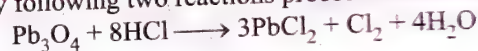
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
- $2\text{Pb}(\text{NO}_3)_2(\text{s}) \longrightarrow 2\text{PbO}(\text{s}) + 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$
- $\text{NaH}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$
- $2\text{NO}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \longrightarrow \text{NO}_2^-(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Sol.

- Combination redox reaction:** N_2 and O_2 combines together to give NO (nitric oxide).
- Decomposition redox (nitric oxide):** $\text{Pb}(\text{NO}_3)_2$ (lead nitrate) breaks into three components.
- Displacement redox reaction:** Hydrogen of H_2O is displaced by H^- (hydride ion) into H_2 gas.
- Disproportionation redox reaction:** NO_2 (+4 oxidation state) disproportionates into NO_2^- (+3 oxidation state) and NO_3^- (+5 oxidation state).

ILLUSTRATION 2.6

Why following two reactions proceed differently?

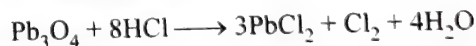


and

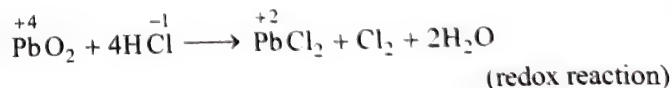
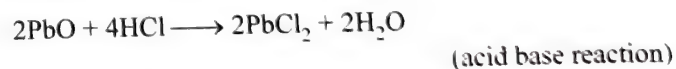


Sol. Pb_3O_4 is a mixed oxide of $(\text{PbO}_2 + 2\text{PbO})$. In PbO_2 , Pb is in +4 oxidation state and the stable oxidation state of Pb in PbO is +2. PbO_2 thus acts as an oxidising agent (oxidant) and therefore can oxidise Cl^- ion of HCl into Cl_2 . Moreover, PbO is a basic oxide.

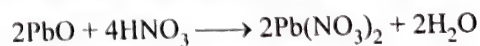
Thus, the reaction



is split into two reactions as follows:



Reaction between PbO_2 and HNO_3 does not occur since HNO_3 is itself an oxidising agent but the acid base reaction between PbO and HNO_3 occurs as follows:



PbO_2 is passive against HNO_3 . That is why the reaction proceeds differently with HCl .

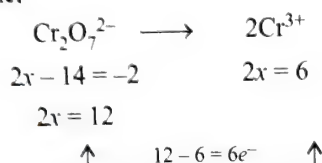
2.13 BALANCING OF REDOX REACTIONS

For balancing of redox reactions, two methods are generally adopted:

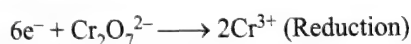
- Oxidation number method
- Ion electron (half reaction) method
- Arbitrary coefficient method

2.13.1 OXIDATION NUMBER METHOD

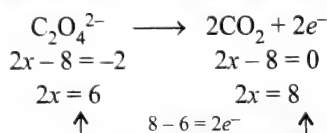
- Write two oxidation and reduction reactions separately, either by involving atoms or ions as such.
- Balance the atom whose oxidation number is changing. For example,



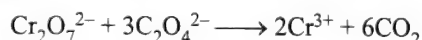
- Add proper number of e^- 's to the side having higher oxidation number



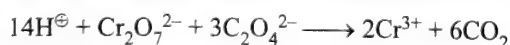
- Similarly balance oxidation half equation, e.g.,



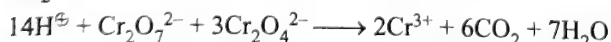
- Now equalise the number of e^- 's in both oxidation and reduction half equation by multiplying with proper number and add them, e.g., multiply Eq. (iv) by 3 and add Eqs. (iii) and (iv)



- Now balance the charge on both sides by adding proper number of H^+ ions (in acidic medium) or OH^- ions (in basic medium). For example in Eq. (v), total charge on LHS is -8 and total charge on RHS is $+6$. So add 14H^+ to LHS.



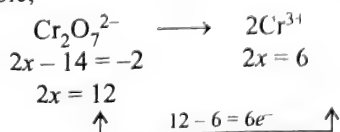
- Balance the O atoms by adding proper number of H_2O molecule to the side deficient of H atoms. For example add $7\text{H}_2\text{O}$ to RHS.



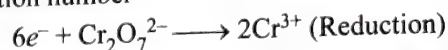
This is a balanced redox equation (check total charge and all atoms are balanced on both sides).

2.13.2 ION ELECTRON (HALF REACTION) METHOD

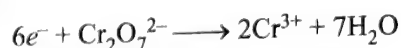
- Balance both oxidation and reduction half equations completely in respect of charge and atoms.
- Balancing of reduction half equation.
- Balance the atom whose oxidation number is changing. For example,



- Add proper number of e^- 's to the side having higher oxidation number

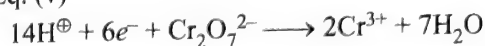


- Balance O atoms by adding proper number of H_2O molecule to the side deficient of O atoms, e.g., add $7\text{H}_2\text{O}$ to RHS in Eq. (iv)



- Balance H atoms:

- In acidic medium: Add proper number of H^+ ions to the side deficient of H atoms e.g., add 14H^+ ions to LHS in Eq. (v)

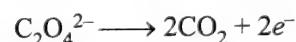


This is a balanced reduction half equation. (Check total charge and all atoms are balanced on both sides).

- In basic medium: Add proper number of H_2O molecules to the side deficient of H atoms and simultaneously add

same number of OH^- ions to the other side.

- Proceeding in same way, balance oxidation half equation, e.g.,



- Now equalise the number of e^- 's in both oxidation and reduction half equation by multiplying with proper number and add them to get final redox equation e.g., multiply Eq. (vii) by 3 and add Eqs. (vi) and (vii).

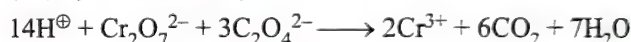
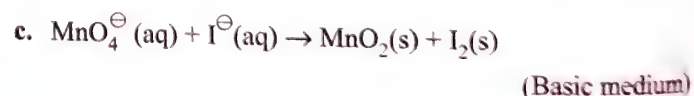
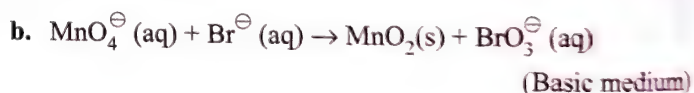
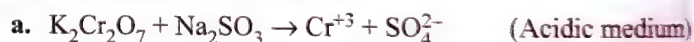
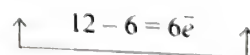
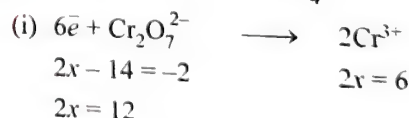
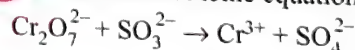


ILLUSTRATION 2.7

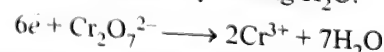
Write the balanced ionic equation



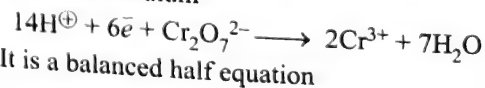
Sol. a. The skeletal ionic equation is:



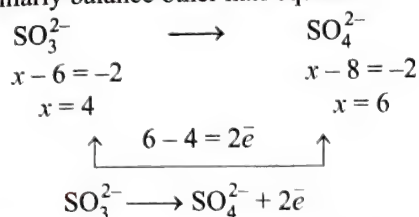
- Balance for O atoms by adding H_2O .



- Balance H atoms by adding proper number of H^+ ions for acidic medium



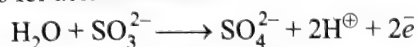
(iv) Similarly balance other half equation



(v) Balance for O atoms by adding proper number of H_2O .

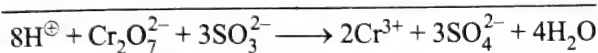
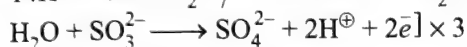
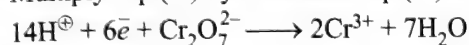


(vi) Balance for H-atoms by adding proper number of H^+ ions for acidic medium.



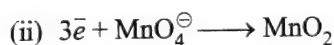
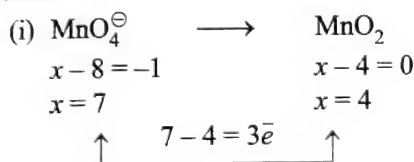
It is a balanced half equation.

(vii) Multiply Eq. (vi) by 3 and add Eq. (iii) to it.

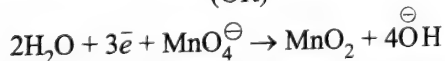
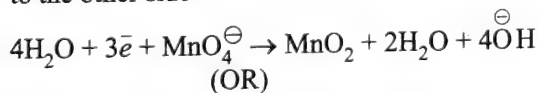


It is a balanced equation.

b. Proceed in same manner in part (a) above two equations are balanced.

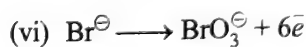
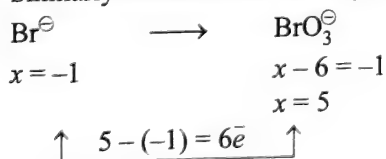


(iv) For balancing of H atoms in basic medium add proper number of H_2O molecules to the side deficient of H atoms and simultaneously add same number of OH^- to the other side

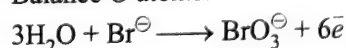


It is a balanced half equation in basic medium.

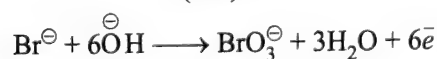
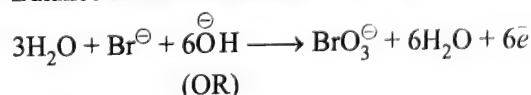
(v) Similarly balance other half equation



(vii) Balance O atoms:

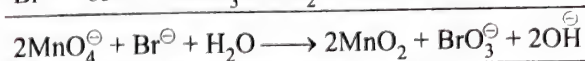
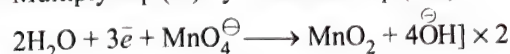


(viii) Balance H atoms in basic medium.



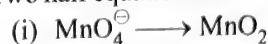
It is a balanced half equation.

(ix) Multiply Eq. (iv) by 2 and add Eq. (viii)

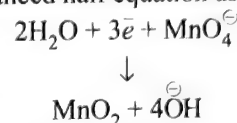


It is a balanced equation.

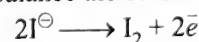
c. Proceeding in the same manner as in part (a) and (b) above. Two half equations are balanced in basic medium as below:



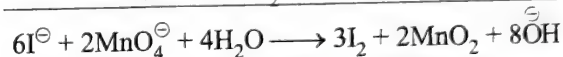
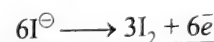
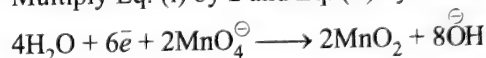
The balanced half equation as in part (b) is:



(ii) Similarly balance the other half equation.



Multiply Eq. (i) by 2 and Eq. (ii) by 3 and add them:



It is a balanced equation.

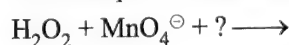
2.13.3 COMPARISON OF ION ELECTRON AND OXIDATION NUMBER METHODS OF BALANCING EQUATIONS

Both methods lead to correct form of the balanced equation.

There are two advantages of ion-electron method:

a. It differentiates those components of a system that react from those that do not.

For example, in the reaction



Any MnO_4^- [KMnO_4 + NaMnO_4 or $\text{Ca}(\text{MnO}_4)_2$] or any strong acid ($(\text{H}^+)_2\text{SO}_4^{2-}$, H^+ClO_4^- but not H^+Cl^-) can be used. The use of complete formulas for neutral substances is helpful only for the calculation of mass relationship. Choose any permanganate, e.g., KMnO_4 , and weigh an amount of KMnO_4 which will give the correct weight of MnO_4^- .

b. The half equations given by ion electron method can be made to occur independently, e.g., in electrochemical cell for producing an electrical potential.

Some chemists prefer the ion electron method for redox reactions carried out in dilute aqueous solutions, where free ions have more or less independent existence. Whereas the oxidation number method for redox reaction is used mainly for the reactions between solid chemicals or for reactions carried out in concentrated acid medium.

2.14 REDOX REACTIONS AS THE BASIS FOR TITRATIONS

In acid-base titration, an acid is titrated against a base by using a suitable indicator, such as phenolphthalein or methyl orange to find the end point. The acid-base titration is used to know the exact amount of an acid or a base present in the given solution by

titrating it with the solution of standard base (or acid). A standard solution is that whose exact molarity or normality is known, which is determined by weighing the exact amount of the substance followed by making its solution.

Similarly, redox titrations are used to determine the exact amount of an oxidising (or a reducing) agent in a given solution by titrating it with the standard solution of a suitable reducing agent (or the oxidising agent).

These two types of titrations differ from each other based on the choice of indicators.

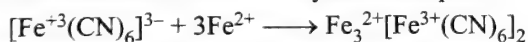
Self-indicator: Acid-base indicators are not useful for redox titrations. In redox reactions, indicators are selected from one of the reagents which itself is coloured, for example, KMnO_4 or MnO_4^- acts as the *self-indicator*.

In the titration of KMnO_4 vs Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$ ions, when whole of the reductant (Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$) is oxidised, the end point is obtained. At this point, the violet colour of MnO_4^- solution disappears and pink colour appears. The change in colour is very sensitive ions even at very low concentration of MnO_4^- ions.

Internal indicator: When there is no auto colour change (as with KMnO_4 titration), different indicators are used which are immediately oxidised after the last drop of reactant (Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$) reacts giving colour change. In the titration of $\text{Cr}_2\text{O}_7^{2-}$ vs. Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$ ions, $\text{K}_2\text{Cr}_2\text{O}_7$ is not a self indicator, so 1% solution of diphenyl amine and syrupy acid (H_3PO_4) is used. At the end point, there is change of colour from green (due to the formation of chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3$) to blue-violet which persists on shaking.

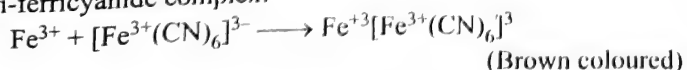
External indicator: 0.1% solution of potassium ferri-cyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$, acts as an external indicator in redox titration, e.g., $\text{K}_2\text{Cr}_2\text{O}_7$ vs. Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$ ions. Freshly prepared potassium ferricyanide solution is used since the old sample of it is contaminated with potassium ferrocyanide, $\text{K}_4[\text{Fe}(\text{CN})_6]$.

As the reaction proceeds, a strong blue colour is developed due to the formation of ferro-ferricyanide complex.

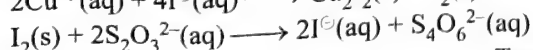
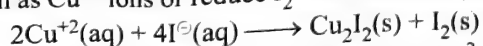


This blue colour can also be developed inside the reaction beaker but as the solution becomes green due to the formation of $\text{Cr}_2(\text{SO}_4)_3$, the exact point of the appearance of blue colour is obscured. To avoid it, the indicator is used externally. The drop of indicator is placed on white tile and from time to time during the titration of $\text{K}_2\text{Cr}_2\text{O}_7$ with Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$ ions, a drop of solution from the titration flask is taken out and added to the indicator.

As the titration proceeds, the blue colour becomes fainter. When a drop of solution produces no change in the colour of the indicator's drop, this becomes the end point, i.e., oxidation of Fe^{2+} to Fe^{3+} has completed. At the end point, the colour of the indicator's drop becomes *light brownish yellow* due to the reaction of indicator with Fe^{3+} ions to produce brown coloured ferri-ferricyanide complex.



Starch indicator: The use of this indicator is, however, limited to only those reagents which can either oxidise I^- ions such as Cu^{2+} ions or reduce I_2 such as thiosulphate ($\text{S}_2\text{O}_3^{2-}$) ions.

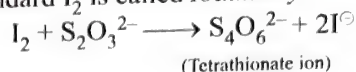


Tetrathionate ion

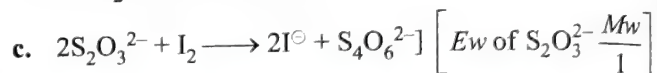
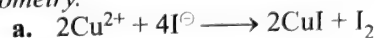
When I^- ions are oxidised to I_2 , *intense blue colour* appears at the end point. When I_2 is reduced to I^- ions, the blue colour disappears at the end point.

Note: I_2 is insoluble in H_2O , but easily soluble in KI solution due to the formation of KI_3 ($\text{I}_2 + \text{KI} \rightarrow \text{KI}_3$).

Iodimetry: Estimation of reducing substance by the use of standard I_2 is called *Iodimetry*.



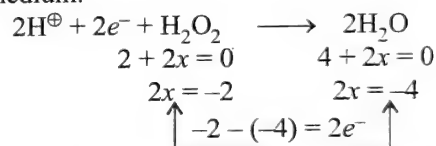
Iodometry: Estimation of oxidising substance involving the liberation of I_2 and subsequent volumetric estimation of I_2 is called *Iodometry*.



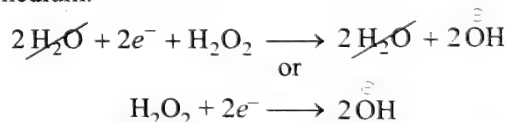
2.15 BALANCING OF H_2O_2 AS OXIDANT AND REDUCTANT IN ACIDIC AND BASIC MEDIUM

H_2O_2 acts both as oxidant (oxidising agent), i.e., undergoes reduction to give H_2O , and as reductant (reducing agent), i.e., undergoes oxidation to give O_2 in both acidic and basic medium as below:

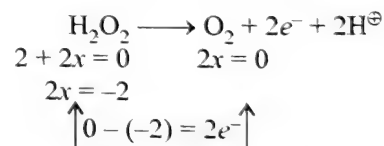
- a. H_2O_2 undergoes reduction and acts as oxidant in acidic medium.



- b. H_2O_2 undergoes reduction and acts as oxidant in basic medium.



- c. H_2O_2 undergoes oxidation and acts as reductant in acidic medium.



- d. H_2O_2 undergoes oxidation and acts as reductant in basic medium.

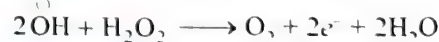


ILLUSTRATION 2.8

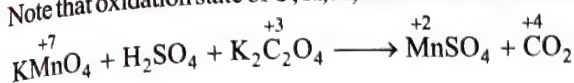
Balance the following reaction by oxidation number and ion electron method:



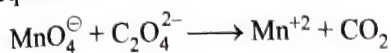
Sol. Oxidation number method:

Follow the steps given below to balance the reaction given above.

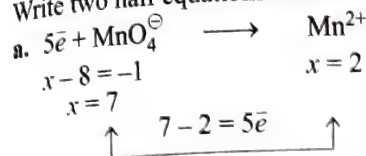
Assign oxidation state to the atoms that are oxidised or reduced.
Note that oxidation state of O, K, H, and S is same on both sides.



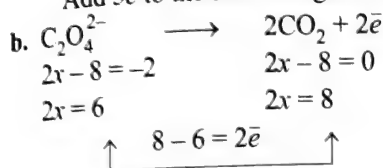
Make ionic equation:



Write two half equations and balance as follows:



Add $5e^-$ to the side of higher O.N. i.e. to the left

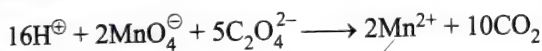


- (i) First balance the C atom whose O.N. is changing
 (ii) Add proper number of electrons to the R.H.S. (higher O.N.)
 c. Add two half equations after multiplying (a) by 2 and (b) by 5 in order that electrons from both sides cancel each other
 $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2$
 d. Balance the charge by adding proper number of H^+ ions in acidic medium

Charge on L.H.S.
= -12

Charge on R.H.S.
+4

So add 16H^+ to L.H.S. to equalise charge on both sides

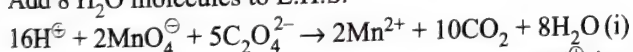


- e. Balance O atoms by adding H_2O molecules to the side deficient of O atom.

O atoms on
L.H.S. = 28

O atoms on
R.H.S. = 20

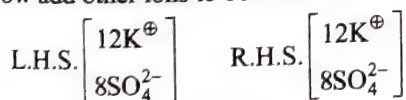
Add 8 H_2O molecules to L.H.S.



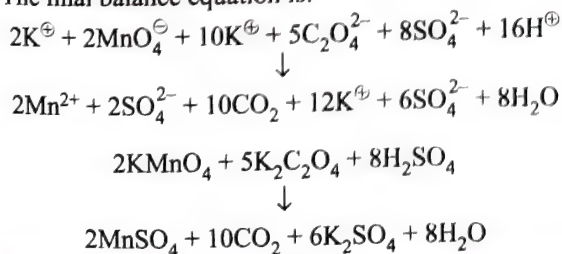
- f. Balance H atoms by adding proper number of H^+ ion (in acidic medium) and OH^- ions in basic medium.

Here H atoms are automatically balanced. Equation (i) is balanced in terms of charge, number of O and H atoms.

- g. Now add other ions to both sides

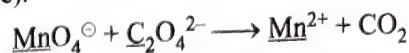


- h. The final balance equation is:



Note: Make a final check by counting O atoms on both sides.

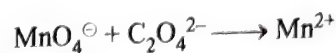
Ion electron method: First write the given equation in ionic form having ions with central atom (which has undergone a change in oxidation state).



Note that O and H atoms attached to the central atom (shown in underlined) have to be retained.

Now, write the oxidation and reduction half reactions and balance them as shown:

Reduction:

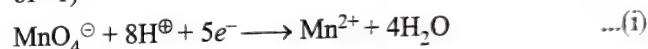


- a. First, make sure that the element undergone the change in oxidation state is balanced.
 b. Balance O atoms by adding $4\text{H}_2\text{O}$ on RHS.
 $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 c. Now, RHS has excess of 8H atoms. Add 8H^+ on LHS. Note, the medium is acidic due to the presence of H_2SO_4 .
 $2\text{MnO}_4^- + 8\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 4\text{H}_2\text{O}$
 d. Now O and H are balanced. Balance the charge on both sides.

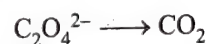
On LHS: Charge is $1 \times (-1) + 8 \times (+1) = +7$

On RHS: Charge is $1 \times (+2) + 4 \times (0) = +2$

Add $5e^-$ in LHS (Note: each e^- is equivalent to a charge of -1)



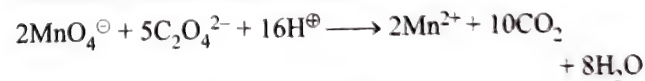
Oxidation:



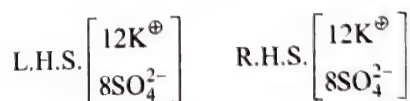
Following the same procedure as above, we have:

- a. Balance C atoms: $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2$
 b. Balance O atoms: Already balanced
 c. Balance H atoms: No H atom
 d. $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^- \quad \dots(\text{ii})$

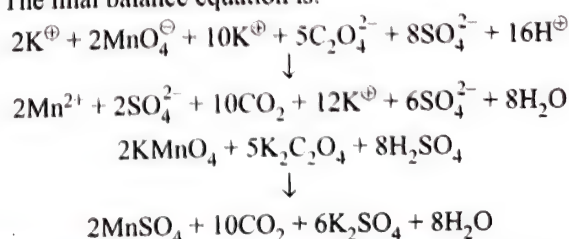
Multiply Eq. (i) by 2 and Eq. (ii) by 5 to balance the electrons transfer and add to get



- e. Now add other ions to both sides



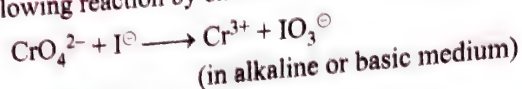
- f. The final balance equation is:



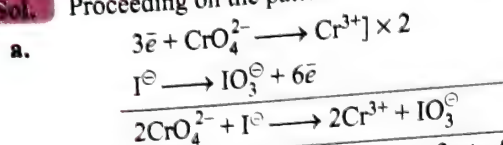
Note: Ion electron method is more important

ILLUSTRATION 2.9

Balance the following reaction by oxidation number method:

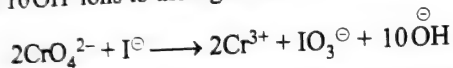


Sol. Proceeding on the pattern of last illustration

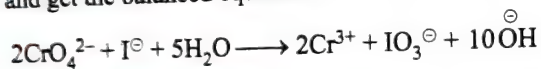


Note that given reaction is ionic, so first of all, the charge needs to be balanced. Balance charge by adding OH^- ions (in basic medium).

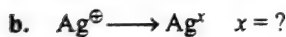
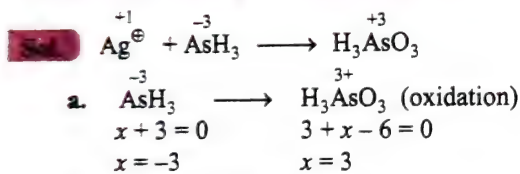
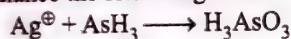
A charge of -5 on the left and $+5$ on the right side means add 10OH^- ions to the right side of the equation.



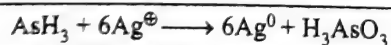
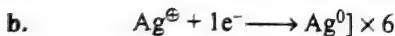
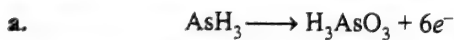
Finally add $5\text{H}_2\text{O}$ molecules on the left to balance H and O and get the balanced equation.

**ILLUSTRATION 2.10**

Complete and balance the following in acidic medium:



Clearly, (b) must be a reduction, so x must be 0, as x cannot be negative for Ag (silver being metal).



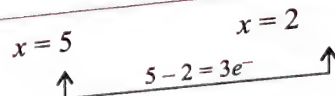
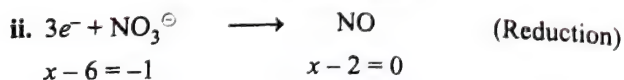
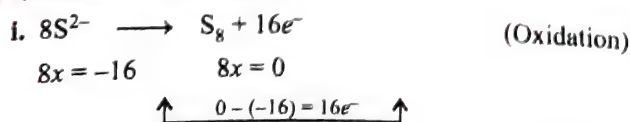
Now balance charge by adding 6H^+ on right side and finally add $3\text{H}_2\text{O}$ on left side.

**ILLUSTRATION 2.11**

Balance the following reaction in acidic medium.



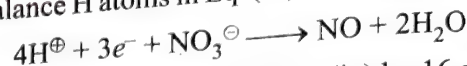
Sol. (Ion electron method)



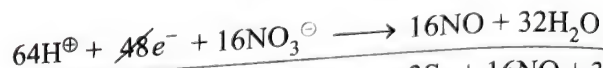
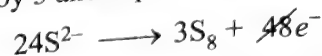
iii. Balance O atoms in Eq. (ii) by adding $2\text{H}_2\text{O}$ to RHS



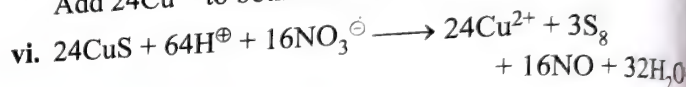
iv. Balance H atoms in Eq. (iii) by adding 4H^+ ions to LHS



v. Multiply Eq. (i) by 3 and Eq. (iv) by 16 and add them



Add 24Cu^{2+} to both sides.



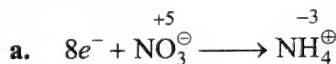
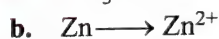
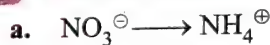
Equation (vi) is the net redox equation.

ILLUSTRATION 2.12

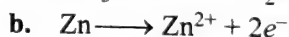
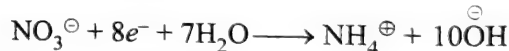
Balance the following by ion electron method in basic medium.



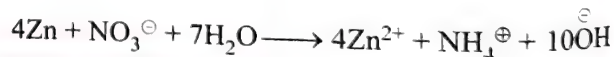
Sol. Two half reactions are



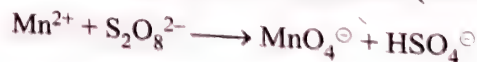
Balance O atom by adding $3\text{H}_2\text{O}$ to R.H.S. and for balancing H atoms in basic medium add $10\text{H}_2\text{O}$ to L.H.S. and add 10OH^- ions to R.H.S. net equation is



Now overall reaction is

**ILLUSTRATION 2.13**

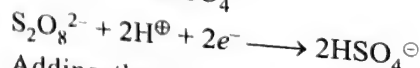
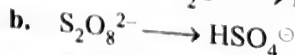
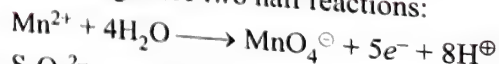
Balance the following by ion electron method (acidic medium):



Sol. Two half reactions are



Balancing these two half reactions:



Adding the two equations, we have the balanced equation.

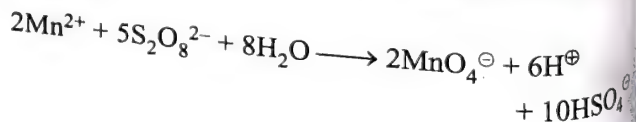
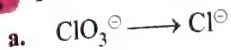


ILLUSTRATION 2.14

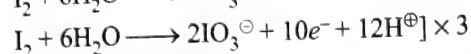
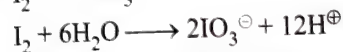
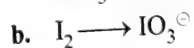
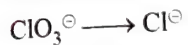
Balance the following by ion electron method in acidic medium.



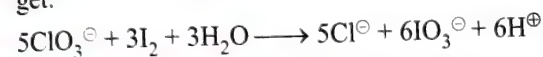
Sol. Two half reactions are



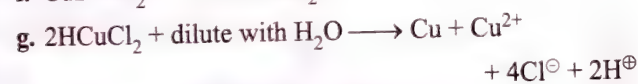
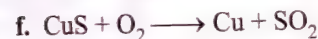
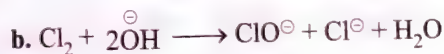
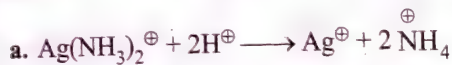
Balancing them separately:



Balance electrons in two half reactions, and adding we get:

**ILLUSTRATION 2.15**

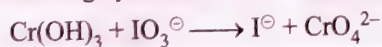
Which of the following are examples of disproportionation reactions?



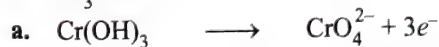
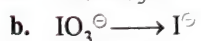
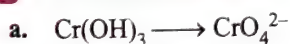
Sol. A reaction in which same atom is oxidised and reduced at the same time is called as a disproportionation reaction. (b), (e), (g), and (h) are disproportionation reactions.

ILLUSTRATION 2.16

Balance the following by ion electron method (basic medium):



Sol. Two half reactions are:



$$x - 3 = 0$$

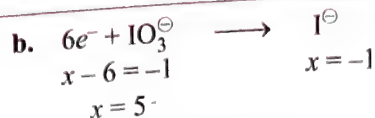
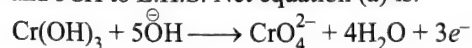
$$x = 3$$

$$x - 8 = -2$$

$$x = 6$$

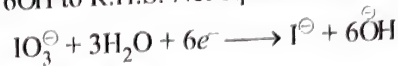
$$\uparrow \quad 6 - 3 = 3e^- \quad \uparrow$$

Balance O atoms by adding one H_2O to L.H.S. For balancing H atoms in basic medium add $5\text{H}_2\text{O}$ to R.H.S. and 5OH^- to L.H.S. Net equation (a) is:

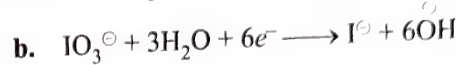


$$\uparrow \quad 5 - (-1) = 6e^- \quad \uparrow$$

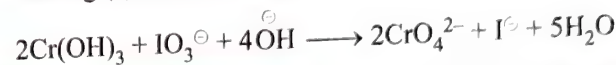
Balance O atoms by adding $3\text{H}_2\text{O}$ to R.H.S. for balancing H-atoms in basic medium add $6\text{H}_2\text{O}$ to L.H.S. and 6OH^- to R.H.S. Net equation (b) is:



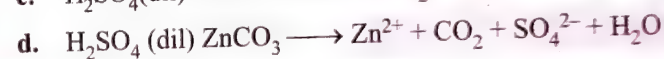
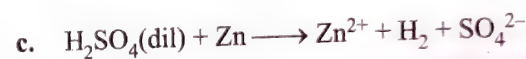
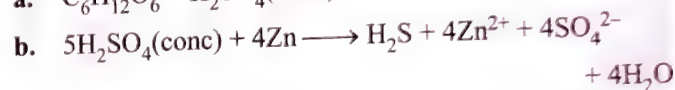
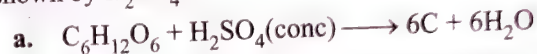
Balancing the charge:



Adding (a) and (b), we get

**ILLUSTRATION 2.17**

H_2SO_4 acts as an oxidising agent, a dehydrating agent, and an acid. Among each of the following reactions, which behaviour is shown by H_2SO_4 ?



Sol.

a. As a dehydrating agent, since it simply removes water from glucose.

b. H_2SO_4 (S in +6 state) $\longrightarrow \text{H}_2\text{S}$ (S in -2 state), i.e., acid is reduced. So it acts as an oxidising agent.

c. All strong acids liberate H_2 with active metals such as Zn (i.e., it is reduced) unless SO_4^{2-} is reduced. In this case, H^+ is reduced to H_2 . So it acts as an oxidising agent. We can also call it as an acidic property.

d. Simply an acid.

ILLUSTRATION 2.18

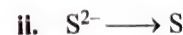
Balance the following reaction by ion electron method (acidic medium):



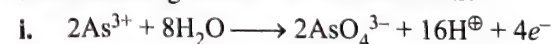
Sol. This is a very special case of redox reaction.

Note that the given reaction involves two oxidations and one reduction.

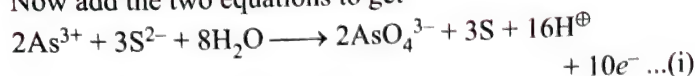
a. Two oxidation half reactions are



First balancing these two half reductions:

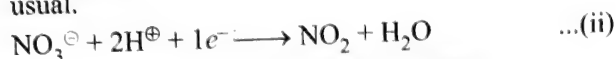


Now add the two equations to get

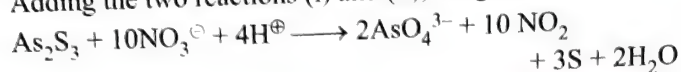


b. Reduction half reaction: $\text{NO}_3^{\ominus} \longrightarrow \text{NO}_2$

Now balance the reduction half reaction and proceed as usual.



Adding the two reactions (i) and (ii), we get



Note: In the above type of cases, take total change in oxidation number (increase or decrease) for cross multiplication while adding oxidation and reduction half reactions. For example, in the given case, 10 electrons are lost per mole of As_2S_3 .

ILLUSTRATION 2.19

For the reaction

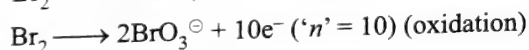
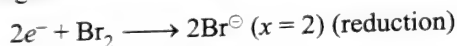


Equivalent weight of Br_2 (molecular weight M) is

a. $\frac{M}{2}$ b. $\frac{M}{10}$ c. $\left(\frac{M}{2} + \frac{M}{10}\right)$ d. $\left(\frac{M}{6}\right)$

Sol.

c. Br_2 disproportionates (simultaneous oxidation and reduction), its equivalent weight is the sum of equivalent weights of the two half reactions.

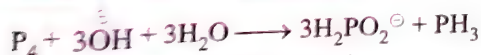


$$2x = 0 \quad 2x - 12 = -2$$

$$2x = 10$$

$$\therefore Ew = \frac{M}{2} + \frac{M}{10} = \left(\frac{80 \times 2}{2} + \frac{80 \times 2}{10}\right) = 96$$

ILLUSTRATION 2.20

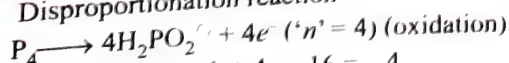


Equivalent weight of P_4 is

a. $\frac{M}{4}$ b. $\frac{M}{12}$
c. $\left(\frac{M}{4} + \frac{M}{12}\right)$ d. $\left(\frac{M}{2} + \frac{M}{6}\right)$

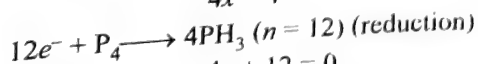
Sol.

c. Disproportionation reaction



$$4x = 0 \quad 8 + 4x - 16 = -4$$

$$4x = 4$$



$$4x = 0 \quad 4x + 12 = 0$$

$$4x = -12$$

$$Ew = \frac{M}{4} + \frac{M}{12} = \left(\frac{31 \times 4}{4} + \frac{31 \times 4}{12}\right) = 41.33$$

ILLUSTRATION 2.21

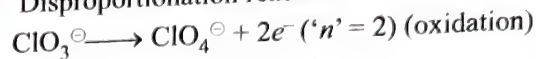


Equivalent weight of KClO_3 is

a. $\frac{M}{4}$ b. $\frac{M}{2}$
c. $\left(M + \frac{M}{2}\right)$ d. $\left(\frac{M}{4} + \frac{M}{2}\right)$

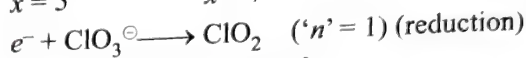
Sol.

c. Disproportionation reaction



$$x - 6 = -1 \quad x - 8 = -1$$

$$x = 5 \quad x = 7$$

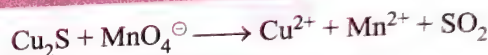


$$x = 5 \quad x - 4 = 0$$

$$x = 4$$

$$Ew = M + \frac{M}{2}$$

ILLUSTRATION 2.22

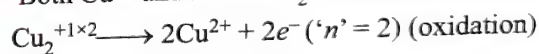


The equivalent weight of Cu_2S is

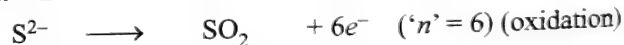
a. $\frac{M}{2}$ b. $\frac{M}{6}$ c. $\frac{M}{8}$ d. $\frac{M}{4}$

Sol.

c. Both Cu^{1+} and S^{2-} in Cu_2S undergo oxidation.



$$2x = 2 \quad 2x = 4$$



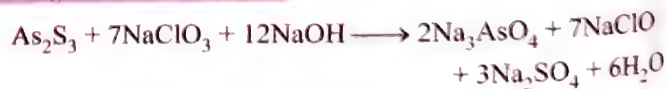
$$x = -2 \quad x - 4 = 0$$

$$x = 4$$

Total $e^- = 8$

$$Ew = \frac{M}{8}$$

ILLUSTRATION 2.23

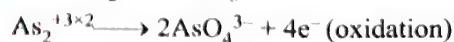


The equivalent weight of As_2S_3 is

a. $\frac{M}{24}$ b. M c. $\frac{M}{2}$ d. $\frac{M}{28}$

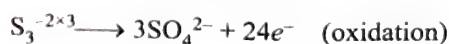
Sol.

d. Both $\text{As}_2^{+3 \times 2}$ and $\text{S}_3^{-2 \times 3}$ undergo oxidation.



$$2x = +6 \quad 2x - 16 = -6$$

$$2x = 10$$



$$3x = -6$$

$$3x - 24 = -6$$

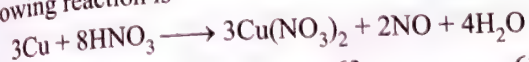
$$3x = 18$$

$$\text{Total } e^- = 24 + 4 = 28$$

$$E_w = \frac{M}{28}$$

ILLUSTRATION 2.24

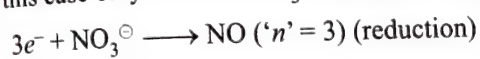
The equivalent weight of HNO_3 (molecular weight = 63) in the following reaction is



- a. $\frac{4 \times 63}{3}$ b. $\frac{63}{5}$ c. $\frac{63}{3}$ d. $\frac{63}{8}$

Sol.

d. In this case only 2 mol of NO_3^- undergo reduction.



$$x - 6 = -1 \quad x - 2 = 0$$

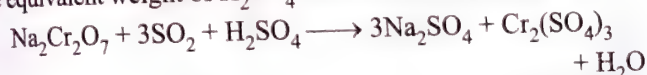
$$x = 5 \quad x = 2$$

6 mol of HNO_3 are not changing so 6NO_3^- are added in the reaction to get 3 mol of $\text{Cu}(\text{NO}_3)_2$.

$$\therefore E_w = M + \frac{M}{3} = \frac{4M}{3} = \frac{4 \times 63}{3}$$

ILLUSTRATION 2.25

The equivalent weight of H_2SO_4 in the following reaction is



- a. 98 b. $\frac{98}{6}$ c. $\frac{98}{2}$ d. $\frac{98}{8}$

Sol.

c. In this reaction, 6 mol of e^- are involved with 1 mol of H_2SO_4 in this redox reaction. H_2SO_4 acts here as acidic medium ('n' = 2), (2H^+) .

$$\text{So, } E_w \text{ of } \text{H}_2\text{SO}_4 = \frac{M}{6} = \frac{98}{2} = 49$$

ILLUSTRATION 2.26

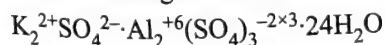
The equivalent weight of potash alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) is

- a. M b. $\frac{M}{2}$ c. $\frac{M}{6}$ d. $\frac{M}{8}$

Sol.

b. Potash alum is a double salt.

$$\text{Total +ve charge} = \text{Total -ve charge}$$



$$\text{Total +ve charge} = 8$$

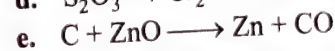
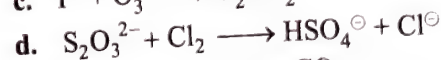
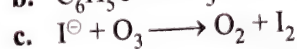
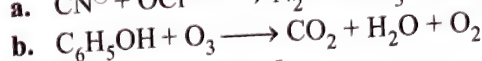
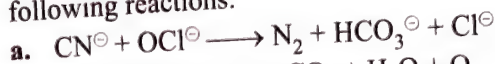
$$\text{Total -ve charge} = 8$$

$$\therefore E_w = \frac{M}{8}$$

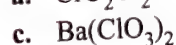
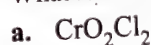
CONCEPT APPLICATION EXERCISE 2.2

Subjective Type

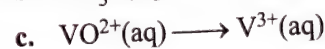
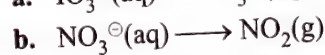
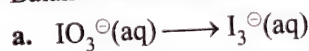
1. Indicate the species which are oxidised and reduced in the following reactions:



2. What is the oxidation state of Cl in



3. Balance the following half-reactions in acidic medium:



4. Write balanced redox reactions for each of the following reactions:

a. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) reacts with hydroiodic acid (HI) to produce potassium iodide, chromium (III) iodide, and solid iodine, $\text{I}_2(\text{s})$.

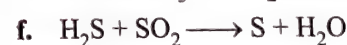
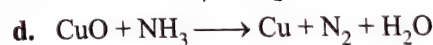
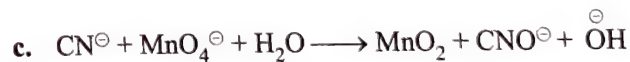
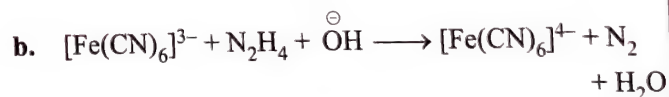
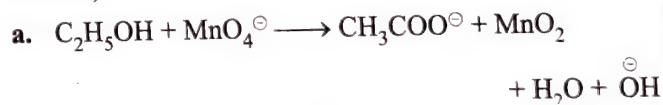
b. A purple solution of aqueous potassium permanganate (KMnO_4) reacts with aqueous sodium sulphite (Na_2SO_3) in basic solution to yield the green manganate ion (MnO_4^{2-}) and sulphate ion (SO_4^{2-}).

c. $\text{Sn}^{2+}(\text{aq})$ reduces $\text{IO}_4^-(\text{aq})$ to $\text{I}^-(\text{aq})$ and is oxidised to Sn^{4+} .

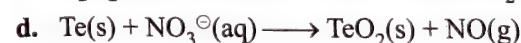
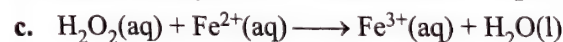
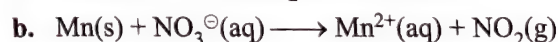
d. $\text{H}_2\text{O}_2(\text{aq})$ oxidises $\text{Mn}^{2+}(\text{aq})$ to MnO_2 in basic medium.

e. $\text{H}_2\text{O}_2(\text{aq})$ reduces $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ to green coloured $\text{Cr}^{3+}(\text{aq})$ in acidic medium.

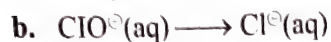
5. Balance the following chemical reactions (by ion electron method)



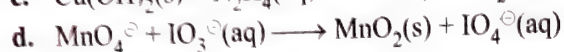
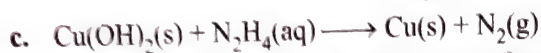
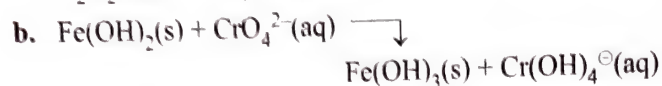
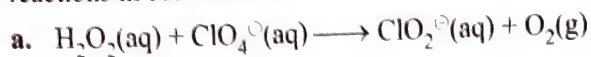
6. Write balanced ionic half equations (oxidation and reduction) for each of the following reactions:



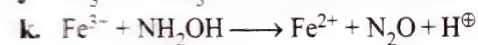
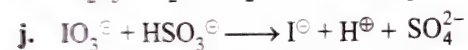
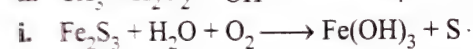
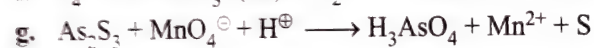
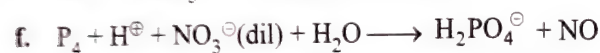
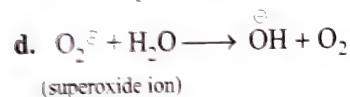
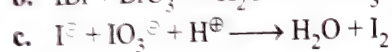
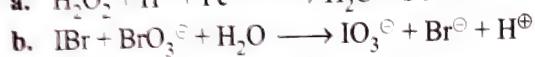
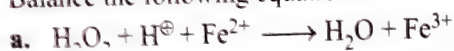
7. Balance the following half reactions in basic medium:



8. Write balanced net ionic equations for the following reactions in basic solution:



9. Balance the following equations:



Objective Type

10. For the redox reaction:



The correct coefficients of the reactants for the balanced reaction are:

	$\text{Cr}_2\text{O}_7^{2-}$	Ni	H^+
(1)	1	3	14
(2)	3	3	12
(3)	2	3	14
(4)	1	1	16

11. SO_2 under atmospheric condition changes to SO_x^{2-} . If oxidation number of S in SO_x^{2-} is +6, what is the value of x in SO_x^{2-} ?

- (1) 2 (2) 1 (3) 3 (4) 4

12. Which of the following can act as an oxidising agent as well as a reducing agent?

- I. H_2O_2 II. H_2S III. SO_2 IV. HNO_2
(1) I, II, III (2) II, III, IV (3) I, III, IV (4) All

13. Sulphur has highest oxidation state in

- (1) SO_2 (2) H_2SO_4
(3) $\text{Na}_2\text{S}_4\text{O}_6$ (4) $\text{Na}_2\text{S}_2\text{O}_3$

14. The number of electrons involved in the reduction of nitrate (NO_3^-) to hydrazine (N_2H_4) is

- (1) 8 (2) 7 (3) 3 (4) 5

15. Oxidation number of P in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is

- (1) +2 (2) +3 (3) +1 (4) -1

16. Which of the following is a disproportionation reaction?



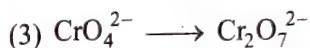
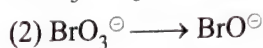
17. In balancing the half reaction



The number of electrons that must be added is

- (1) 1 on the right (2) 0
(3) 1 on the left (4) 2 on the right

18. Which of the following changes requires a reducing agent?



ANSWER KEYS

Subjective Type

1. Refer to solutions.

2. a. -1, b. +7, c. 5, d. +7

Refer to solutions for Q. 3 to 9.

Objective Type

10. (1) 11. (1) 12. (3) 13. (2)

14. (2) 15. (3) 16. (4) 17. (4)

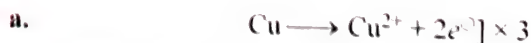
18. (2)

Solved Examples

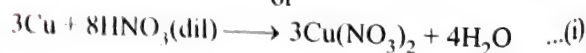
EXAMPLE 2.1

Calculate the number of moles of Cu and HNO_3 to give NO and NO_2 in the (2:1) molar ratio.

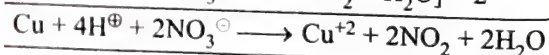
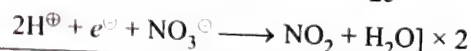
Sol.



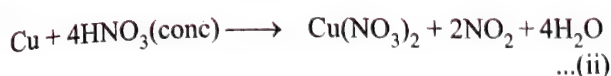
or



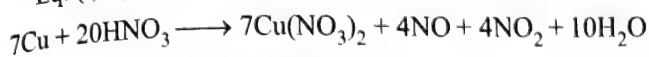
b.



or



To get NO and NO₂ in the molar ratio of 2:1, multiply Eq. (i) by 2 and then add Eqs. (i) and (ii), to get



Hence, number of moles of Cu = 7

Number of moles of HNO₃ = 20

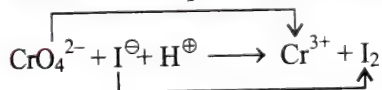
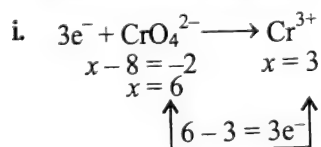
EXAMPLE 2.2

Balance the following equations:

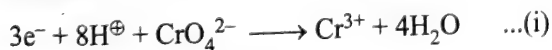
- $\text{BaCrO}_4 + \text{KI} + \text{HCl} \longrightarrow \text{BaCl}_2 + \text{I}_2 + \text{KCl} + \text{CrCl}_3 + \text{H}_2\text{O}$
- $\text{SO}_2 + \text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
- $\text{C}_2\text{H}_5\text{OH} + \text{I}_2 + \text{OH}^\ominus \longrightarrow \text{CHI}_3 + \text{HCO}_2^\ominus + \text{H}_2\text{O} + \text{I}^\ominus \text{ (Basic)}$
- $\text{As}_2\text{S}_3 + \text{HNO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4 + \text{NO}$
- $\dots + \text{HC}_2\text{O}_4^\ominus \longrightarrow \text{CO}_3^{2-} + \text{Cl}^\ominus \text{ (Acidic)}$
- $\text{HgS} + \text{HCl} + \text{HNO}_3 \longrightarrow \text{H}_2\text{HgCl}_4 + \text{NO} + \text{S} + \text{H}_2\text{O}$
- $\text{Mn}_2\text{O}_7 \longrightarrow \text{MnO}_2 + \text{O}_2$

Sol.

- a. First write the equation in ionic form as shown below:

**Ion electron method**

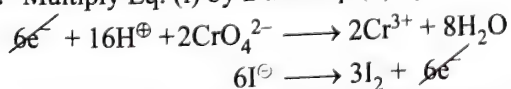
- ii. Balance O atom by adding H₂O to RHS and then balance H atom by adding H⁺ ions (acidic medium) to LHS.



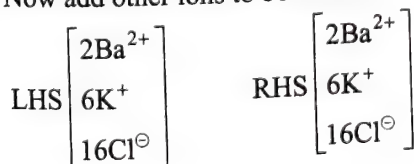
Similarly, balance I[−] to I₂.



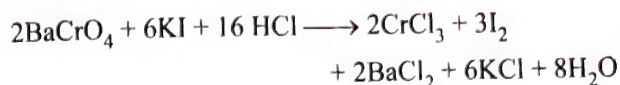
- iii. Multiply Eq. (i) by 2 and Eq. (ii) by 3.



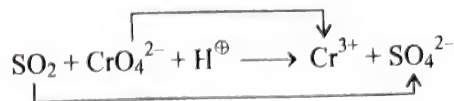
Now add other ions to both sides.



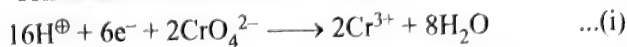
Net equation is



- b. First write the equation in ionic form as shown below:



Ion electron method: (As in (a))

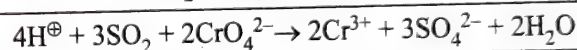
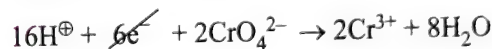


$$x - 4 = 0 \quad x - 8 = -2$$

$$x = 4 \quad x = 6$$

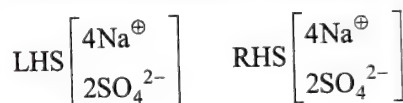
$$\uparrow 6 - 4 = 2\text{e}^- \uparrow$$

Multiply Eq. (ii) by 3 and add Eqs. (i) and (ii)

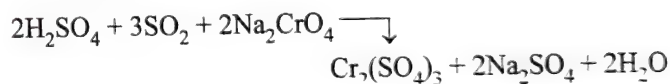


It is a balanced redox equation.

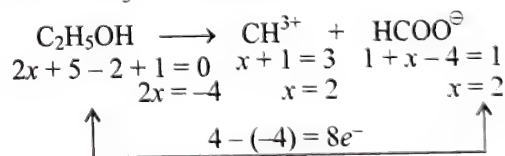
Now add other ions to both sides.



Net equation is:

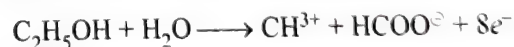


- c. In this reaction, C₂H₅OH is changing to CHI₃ (i.e. CH³⁺ I₃[−]) and HCOO[−] ion.

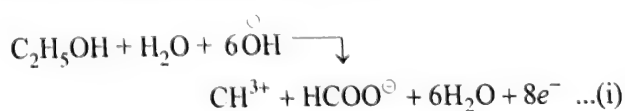


Balance O and H in basic medium.

Balancing of O atom by adding H₂O to LHS



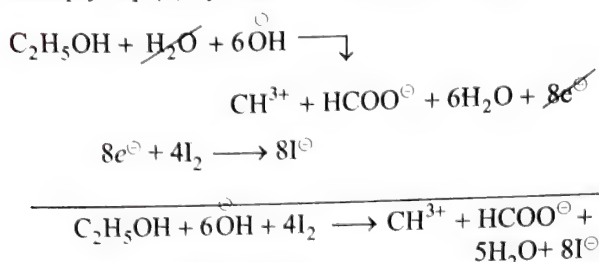
Balancing of H atom by adding 6H₂O to RHS and simultaneously add 6OH[−] to LHS



It is a balanced equation. Similarly, balance the reduction reaction.



Multiply Eq. (ii) by 4 and add Eqs. (i) and (ii)

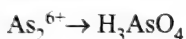


CH^{3+} is combined with 3I^- to form CHI_3 .

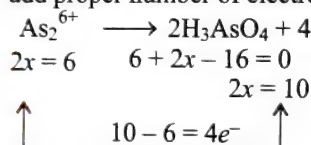
So net balanced equation is:



- d. Here, As_2S_3 (i.e., $\text{As}_2^{+3}\text{S}_3^{-2}$) is split into two parts As_2^{6+} and S_3^{6-} in which As_2^{6+} is oxidised to H_3AsO_4 and S_3^{6-} is also oxidised to SO_4^{2-} (i.e., H_2SO_4)



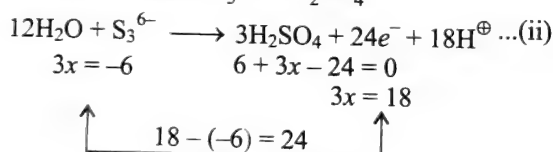
- i. Balance As atom by multiplying RHS by 2 and then add proper number of electrons.



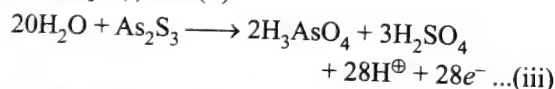
- ii. Balance O and H atoms.



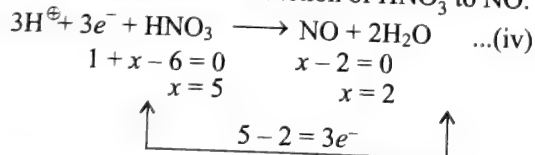
- iii. Similarly, balance S_3^{6-} to H_2SO_4 .



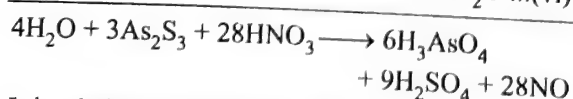
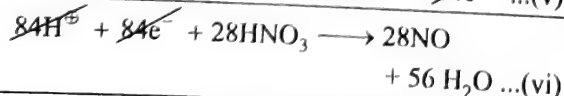
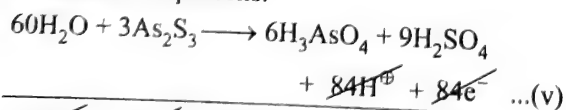
- iv. Add Eqs. (i) and (ii)



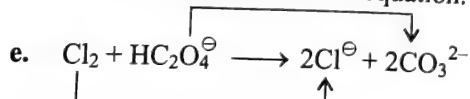
- v. Now balance reduction reaction of HNO_3 to NO .



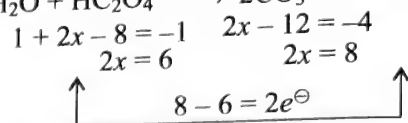
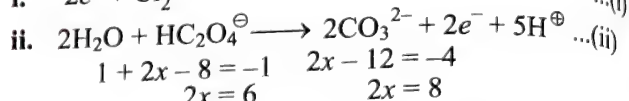
- vi. Multiply Eq. (iii) by 3 and Eq. (iv) by 28 and then add both the equations.



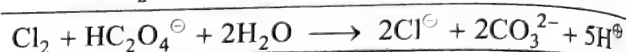
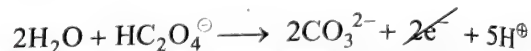
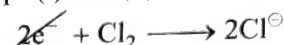
It is a balanced redox equation.



In the blank space on LHS, put Cl_2 ; since HC_2O_4^- is oxidised, therefore Cl_2 is reduced.



Add Eqs. (i) and (ii)

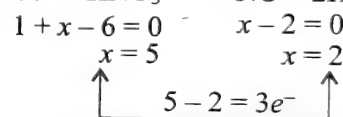
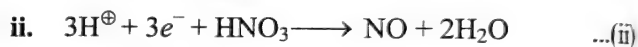
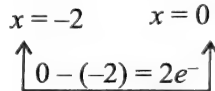
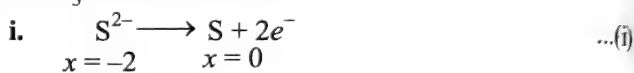


It is a balanced equation.

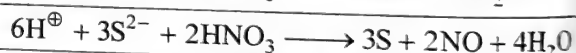
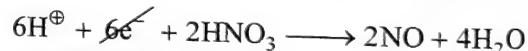
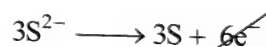
- f. Here, HgS (i.e., $\text{Hg}^{2+}\text{S}^{2-}$) is split into two parts Hg^{2+} and S^{2-} in which only S^{2-} (sulphide ion) is oxidised to



HNO_3 is reduced to NO .

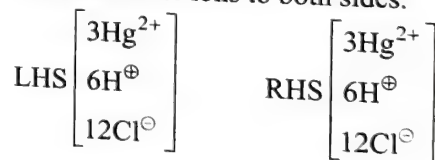


- iii. Multiply Eq. (i) by 3 and Eq. (ii) by 2 and then add both the equations.

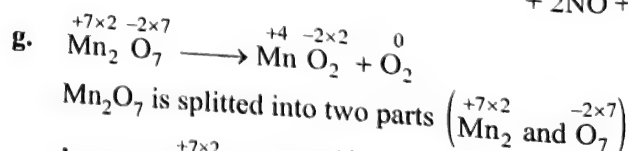
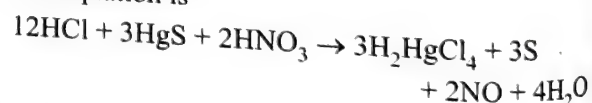


It is balanced equation.

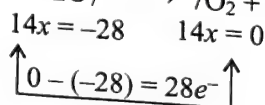
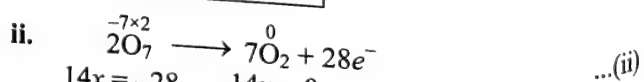
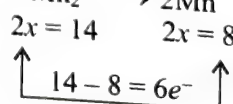
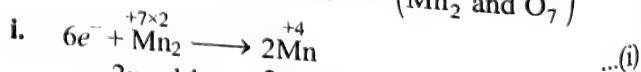
- iv. Now add other ions to both sides.



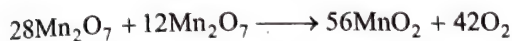
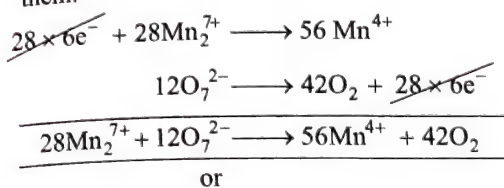
Net equation is



Mn_2O_7 is splitted into two parts (Mn_2 and O_7)



- iii. Multiply Eq. (i) by 28 and Eq. (ii) by 6 and add them.



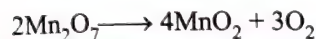
- iv. Balance Mn atom except H and O.



- v. Balance O atom

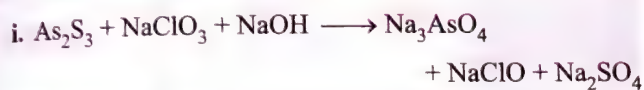


or



EXAMPLE 2.3

Balance the following equations:



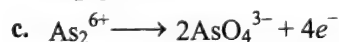
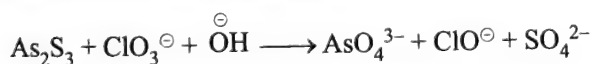
- ii. If M is the molecular mass of As_2S_3 , the equivalent weight of As_2S_3 is

- a. $M/24$ b. M c. $M/2$ d. $M/28$

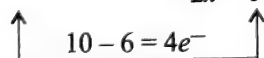
Sol.

- i. a. As_2S_3 is split into two parts $\left(\begin{smallmatrix} +3 \times 2 & -2 \times 3 \\ As_2 & S_3 \end{smallmatrix} \right)$ in which As_2^{6+} is oxidised to AsO_4^{3-} and S_3^{6-} is oxidised to SO_4^{2-} . Whereas, ClO_3^- (Chlorate ion) is reduced to ClO^- (hypochlorite ion).

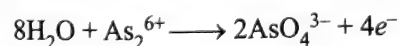
- b. Write the equation in ionic form.



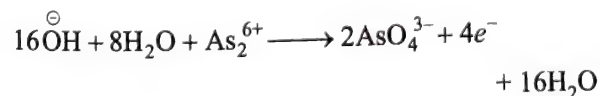
$$\begin{array}{r}
 2x = 6 \quad 2x - 16 = -6 \\
 2x = 10
 \end{array}$$



- d. Balance O atoms by adding $8H_2O$ on LHS.



- e. Balance H atoms in basic medium by adding $16H_2O$ on RHS and simultaneously add $16OH^-$ ions to LHS.

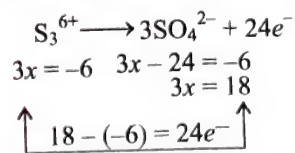


or

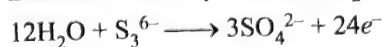


It is a balanced equation.

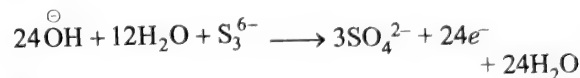
- f. Similarly, balance S_3^{6-} to SO_4^{2-} ion in basic medium.



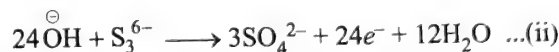
- g. Balance O atom by adding $12H_2O$ on LHS.



- h. Balance H atom in basic medium by adding $24H_2O$ on RHS and simultaneously add $24OH^-$ ions on LHS.

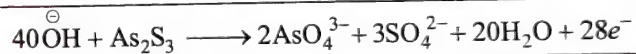
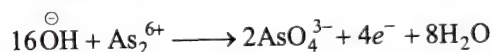


or



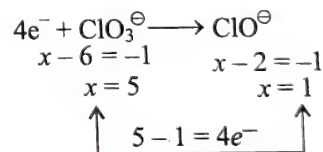
It is a balanced equation.

- i. Now add Eqs. (i) and (ii) to get final oxidation reaction.

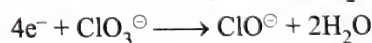


...(iii)

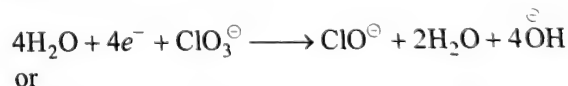
- j. Similarly, balance the reduction equation of ClO_3^- to ClO^- ion.



- k. Balance O atom by adding $2H_2O$ on RHS.



- l. Balance H atoms in basic medium by adding $4H_2O$ on LHS and simultaneously add $4OH^-$ ions on RHS.

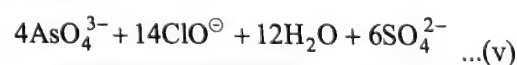
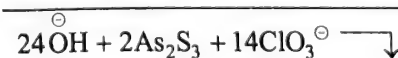
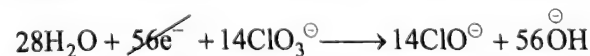
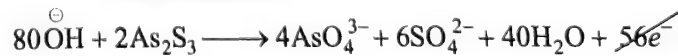


or



It is a balanced reduction equation.

Equation (iii) is an oxidation reaction and Eq. (iv) is a reduction equation. To balance the number of electrons, multiply Eq. (iii) by 2 and Eq. (iv) by 14 and add them.

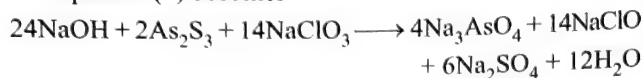


It is a balanced redox reaction.

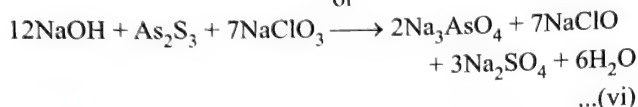
Now add other ions to both sides of Eq. (v).



Equation (v) becomes



or

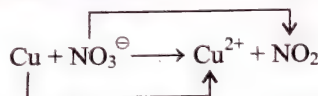


Equation (vi) is the final balanced redox reaction.

- ii. b. The number of electrons involved in Eq. (iii) is 28. So the equivalent weight of As_2S_3 is $M/28$. Answer is (iv).

EXAMPLE 2.4

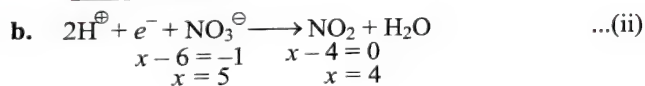
Write a balanced equation when copper reacts with nitric acid, a brown gas is formed and the solution turns blue.



Sol.

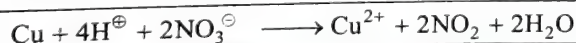
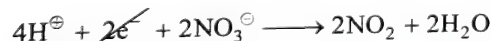
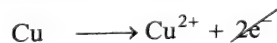


$$\begin{array}{r} x=0 \quad x=2 \\ \uparrow \\ 2-0=2e^- \end{array}$$



$$\begin{array}{r} x-6=-1 \quad x-4=0 \\ x=5 \quad x=4 \\ \uparrow \\ 5-4=1e^- \end{array}$$

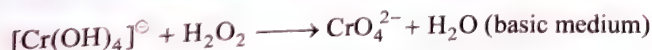
- c. Multiply Eq. (ii) by 2 and add Eqs. (i) and (ii).



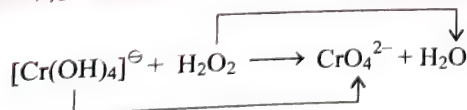
It is a balanced redox equation.

EXAMPLE 2.5

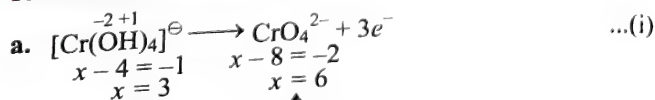
Balance the following redox equation by both methods.



Sol.



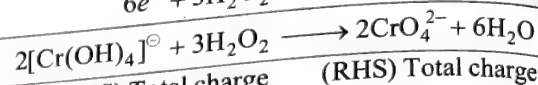
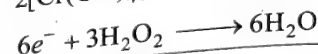
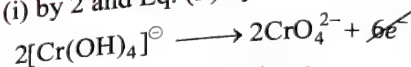
Ion electron method:



$$\begin{array}{r} -2+1 \\ x-4=-1 \quad x-8=-2 \\ x=3 \quad x=6 \\ \uparrow \\ 6-3=3e^- \end{array}$$

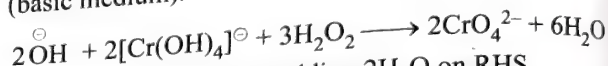


- c. Multiply Eq. (i) by 2 and Eq. (ii) by 3 and add them.

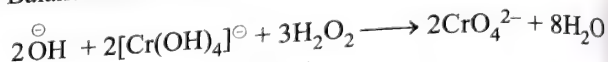


$$\begin{array}{r} \text{(LHS) Total charge} \\ = -2 \end{array} \quad \begin{array}{r} \text{(RHS) Total charge} \\ = -4 \end{array}$$

- d. Balance the charge on both sides by adding 2OH^- on LHS (basic medium).

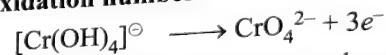


- e. Balance the O atoms by adding $2\text{H}_2\text{O}$ on RHS.



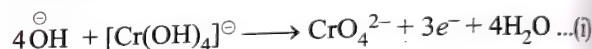
It is a balanced redox reaction.

Oxidation number method:

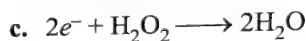


- a. Balance O atoms which are already balanced.

- b. Balance H atoms by adding $4\text{H}_2\text{O}$ to RHS and simultaneously add 4OH^- ions to LHS (basic medium).

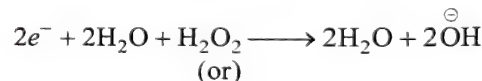


It is a balanced oxidation equation.

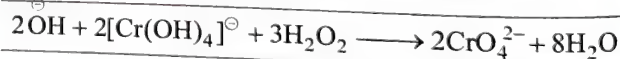
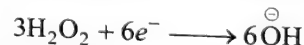
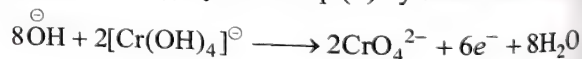


- d. Balance O atoms which are already balanced.

- e. Balance H atoms by adding $2\text{H}_2\text{O}$ to LHS and simultaneously add 2OH^- to RHS.



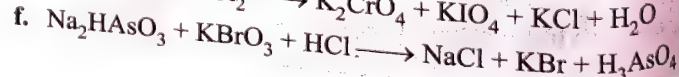
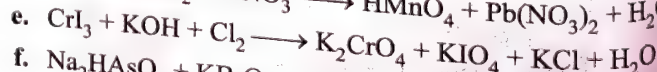
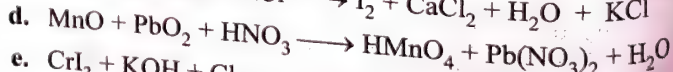
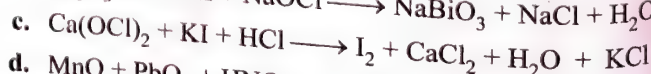
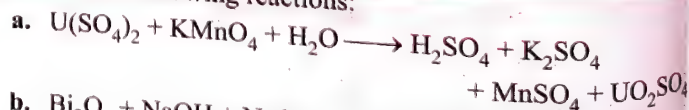
- f. Multiply Eq. (i) by 2 and Eq. (ii) by 3 and add them.

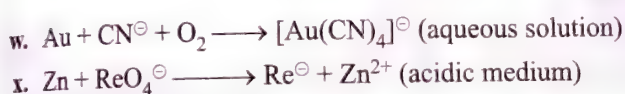
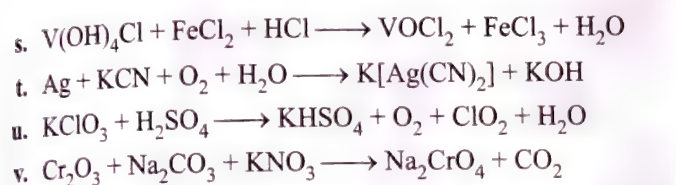
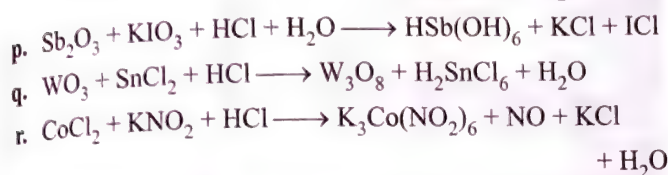
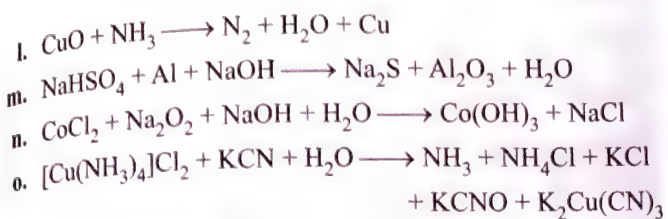
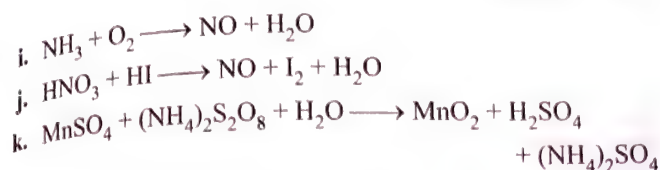
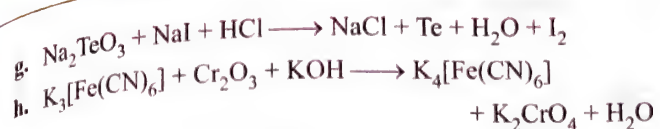


It is a balanced redox reaction, which is same as in ion electron method.

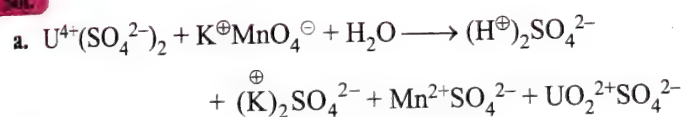
EXAMPLE 2.6

Balance the following reactions:

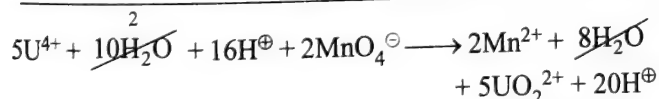
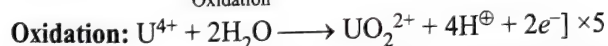
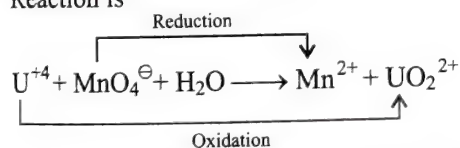




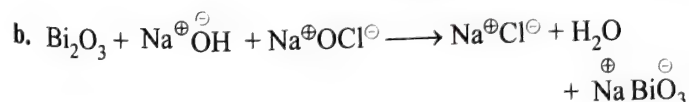
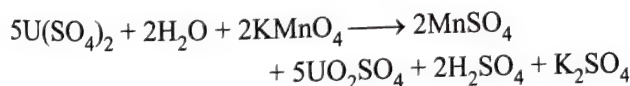
Sol.



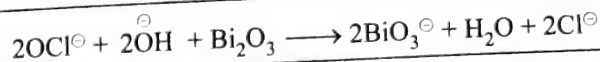
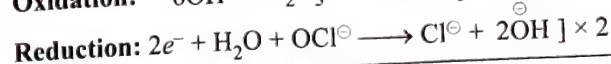
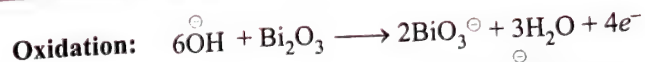
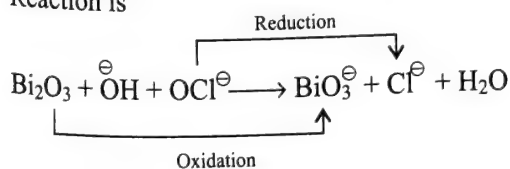
Reaction is



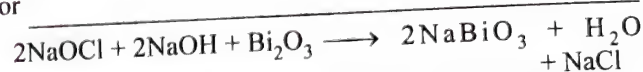
or



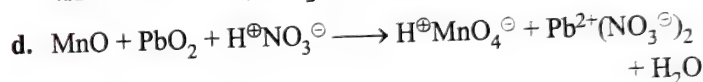
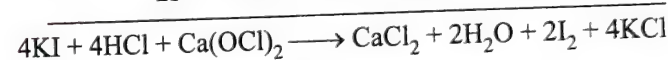
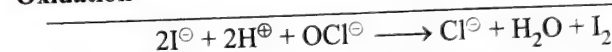
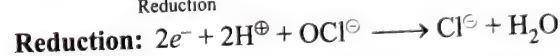
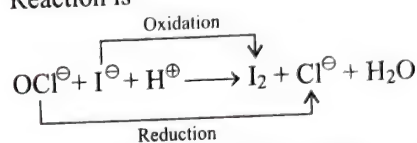
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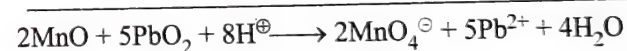
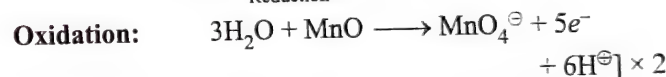
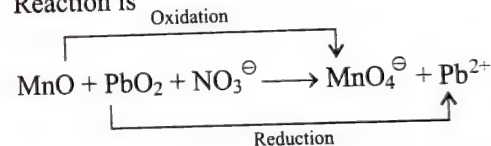
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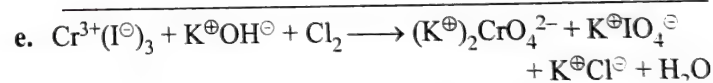
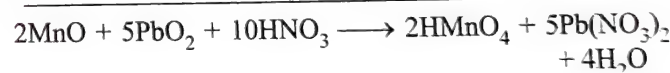
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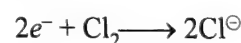
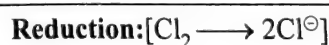
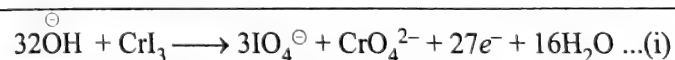
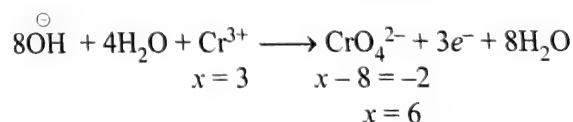
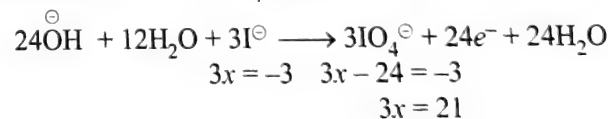
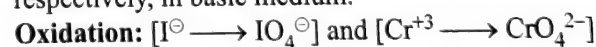
Reaction is



or

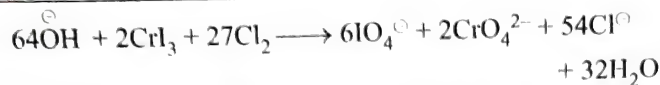


Note that both I^- and Cr^{3+} are oxidised to IO_4^- and CrO_4^{2-} , respectively, in basic medium.

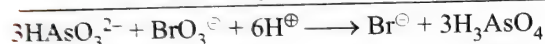
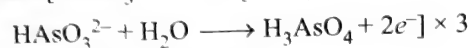
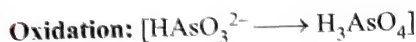
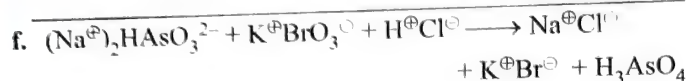
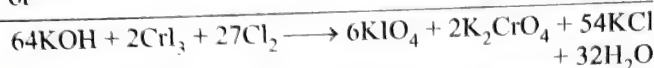


... (ii)

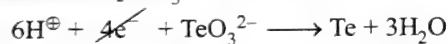
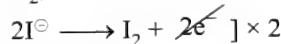
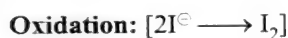
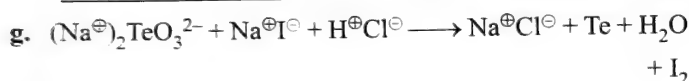
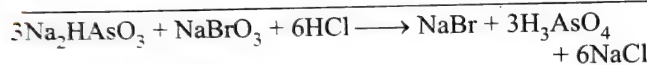
Multiply Eq. (i) by 2 and Eq. (ii) by 27 and add to get final redox equation



or

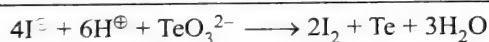


or

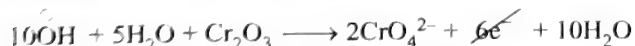
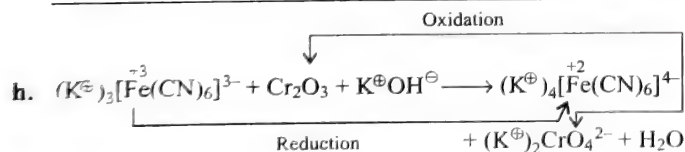
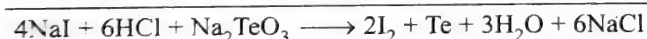


$$x - 6 = -2 \quad x = 0$$

$$x = 4$$



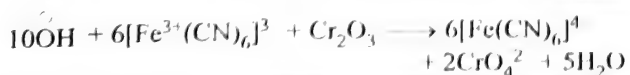
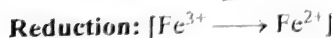
or



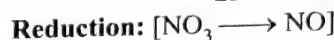
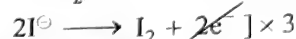
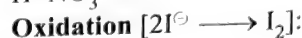
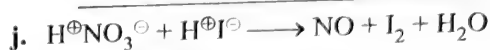
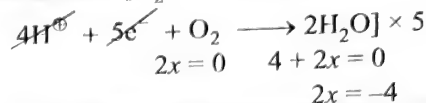
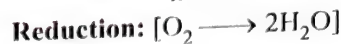
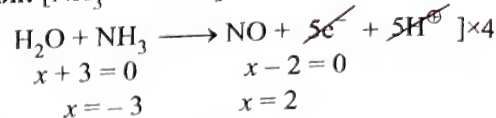
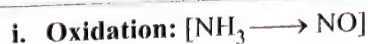
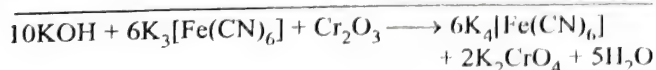
$$2x - 6 = 0 \quad 2x - 16 = -4$$

$$2x = 6$$

$$2x = 12$$

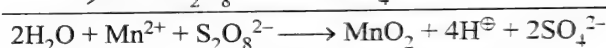
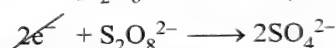
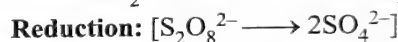
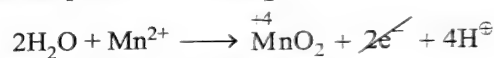
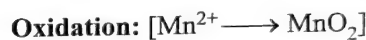
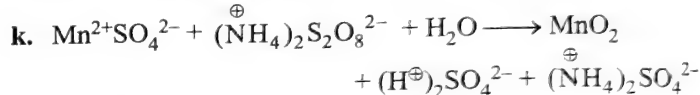


or

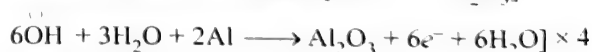
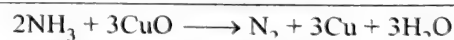
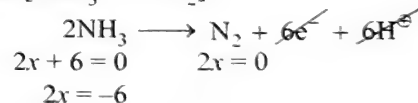
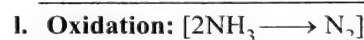
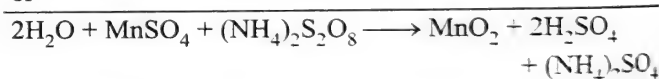


$$x - 6 = -1 \quad x - 2 = 0$$

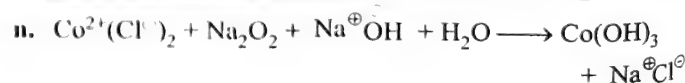
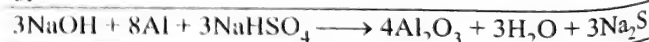
$$x = 5 \quad x = 2$$



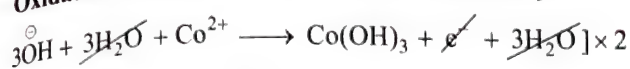
or



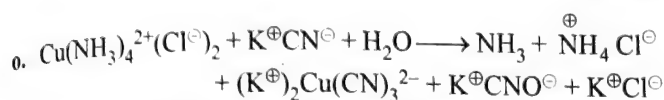
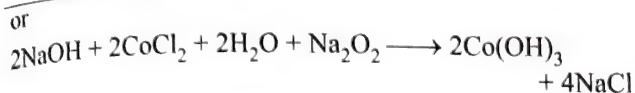
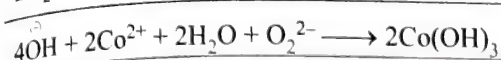
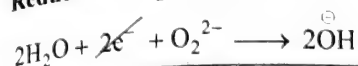
or



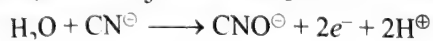
Oxidation (basic medium): $[\text{Co}^{2+} \longrightarrow \text{Co}(\text{OH})_3]$



Reduction: $[\text{O}_2^{2-} \longrightarrow \text{OH}^-]$



Oxidation (basic NH_3 medium): $[\text{CN}^- \longrightarrow \text{CNO}^-]$



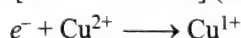
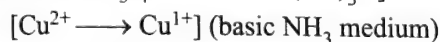
$$x - 3 = -1 \quad x - 3 - 2 = -1$$

$$x = 2 \quad x = 4$$

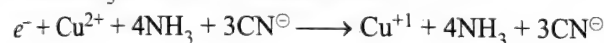
Since the reaction is carried out in NH_3 medium, add 2NH_3 to both sides.



Reduction: $[\text{Cu}^{2+}(\text{NH}_3)_4^{2+} \longrightarrow \text{Cu}^+(\text{CN})_3^{2-}]$



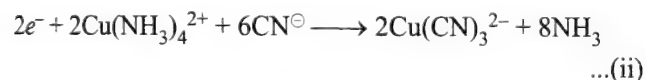
Add 4NH_3 and 3CN^- to both sides.



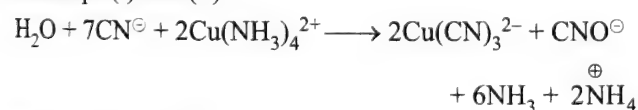
or



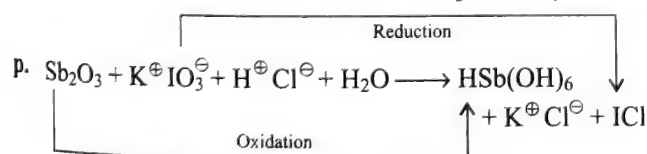
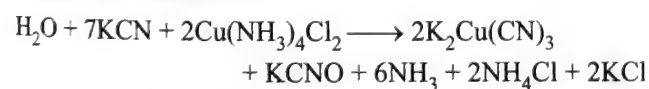
or



Add Eqs. (i) and (ii)



Net redox reaction is



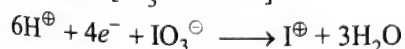
Oxidation: $[\text{Sb}_2\text{O}_3 \longrightarrow 2\text{HSb}(\text{OH})_6]$



$$2x - 6 = 0 \quad 2 + 2x - 12 = 0$$

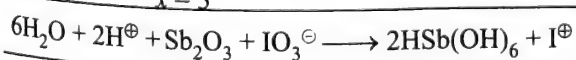
$$2x = 6 \quad 2x = 10$$

Reduction: $[\text{IO}_3^- \longrightarrow \text{I}^+]$

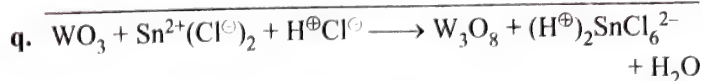
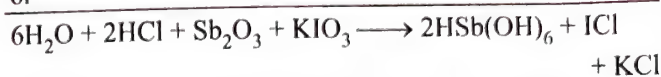


$$x - 6 = -1 \quad x = 1$$

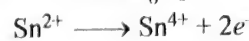
$$x = 5$$



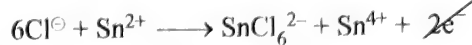
or



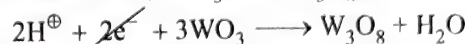
Oxidation: $[\text{Sn}^{2+} \longrightarrow \text{SnCl}_6^{2-}]$



or

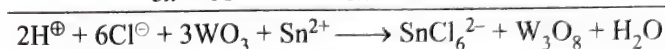


Reduction: $[3\text{WO}_3 \longrightarrow \text{W}_3\text{O}_8]$

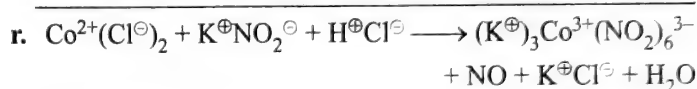
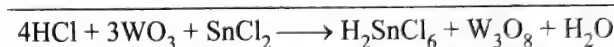


$$3x - 18 = 0 \quad 3x - 16 = 0$$

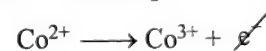
$$3x = 18 \quad 3x = 16$$



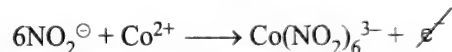
or



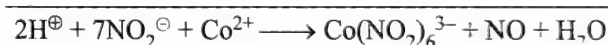
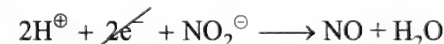
Oxidation: $[\text{Co}^{2+} \longrightarrow \text{Co}^{3+}]$



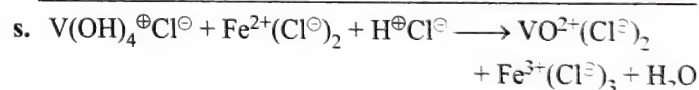
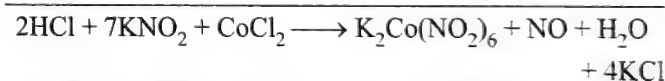
or



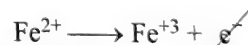
Reduction: $[\text{NO}_2^- \longrightarrow \text{NO}]$



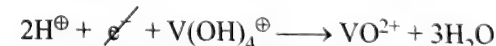
or



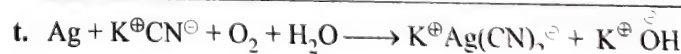
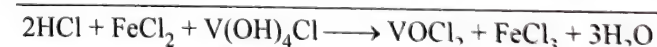
Oxidation: $[\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+}]$



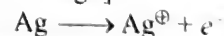
Reduction: $[\text{V}(\text{OH})_4^+ \longrightarrow \text{VO}^{2+}]$



or



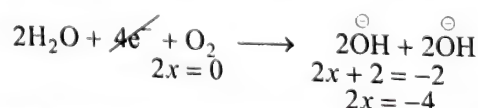
Oxidation: $[\text{Ag} \longrightarrow \text{Ag}^+]$



Add 2CN^- to both sides

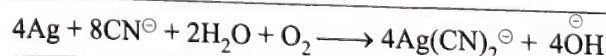


Reduction: $[\text{O}_2 \longrightarrow \text{OH}^-] \text{ (Basic medium)}$

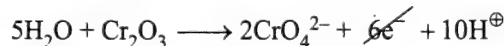
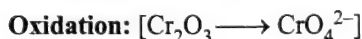
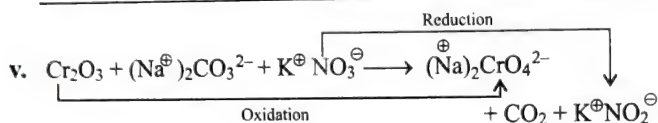
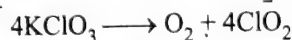
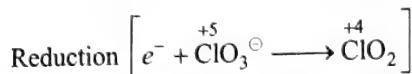
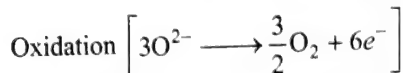
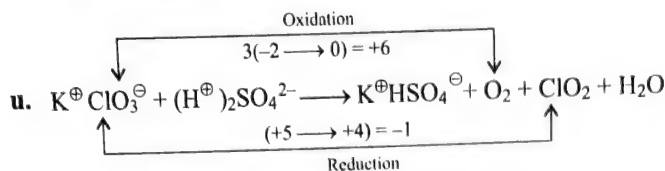
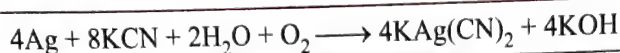


$$2x = 0 \quad 2x + 2 = -2$$

$$2x = -4$$

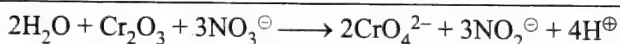
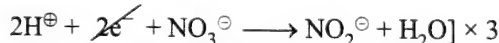
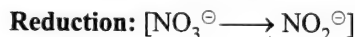
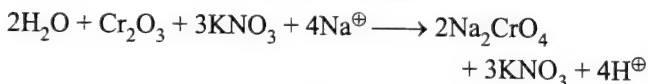
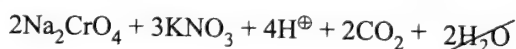
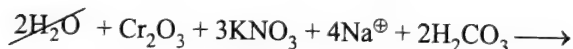
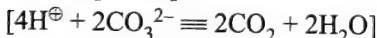


or

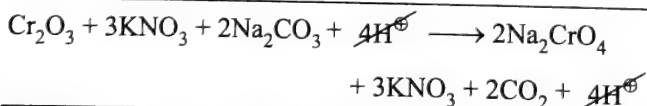


$$2x - 6 = 0 \quad 2x - 16 = -4$$

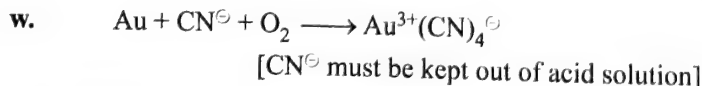
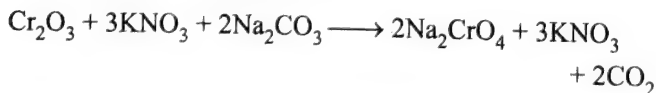
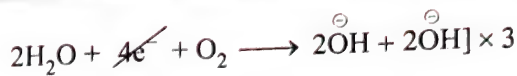
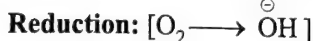
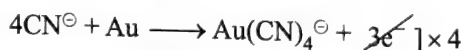
$$2x = 6 \quad 2x = 12$$

Add 3K^+ and 4Na^+ ions to both sides.[Now add $2\text{H}_2\text{CO}_3$ to the left and $2\text{CO}_2 + 2\text{H}_2\text{O}$ to the right of the equation]

or

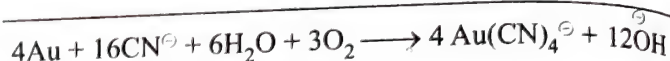


Hence, the net redox reaction is

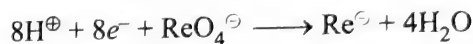
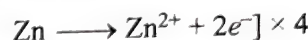
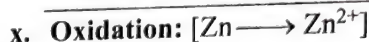
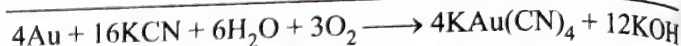
Add 4CN^- both sides

$$2x = 0 \quad 2x + 2 = -2$$

$$2x = -4$$

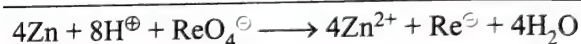


or

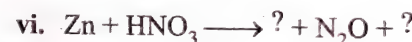
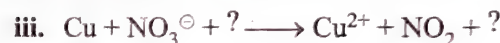
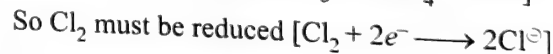
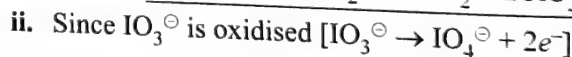
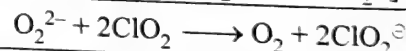
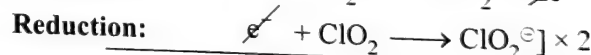
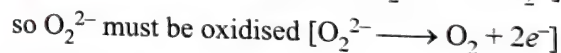
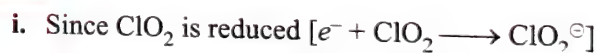
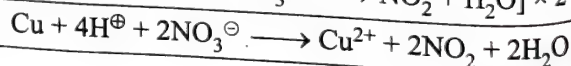
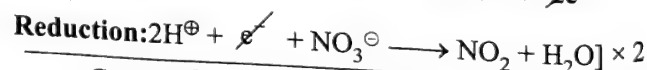
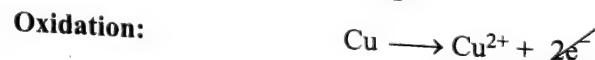
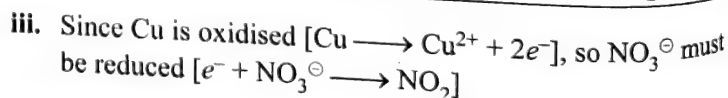
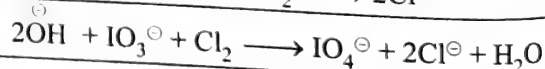
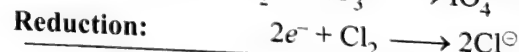
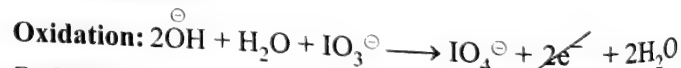


$$x - 8 = -1 \quad x = -1$$

$$x = 7$$

**EXAMPLE 2.7**

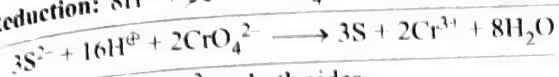
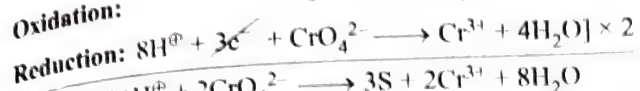
Complete and balance the following equations:

**Sol.****Basic medium:**

iv. Since S^{2-} is oxidised to S [$S^{2-} \rightarrow S + 2e^-$], so CrO_4^{2-} is reduced to Cr^{3+} ($3e^- + CrO_4^{2-} \rightarrow Cr^{3+}$)

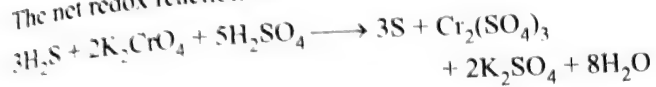


Oxidation:

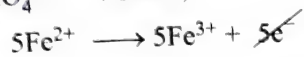
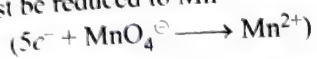


Add, $4K^+$ and $5SO_4^{2-}$ to both sides.

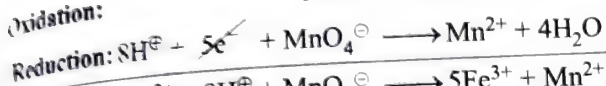
The net redox reaction is



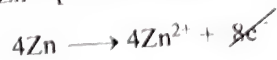
v. Since Fe^{2+} is oxidised to Fe^{3+} ($Fe^{2+} \rightarrow Fe^{3+} + e^-$), so MnO_4^- must be reduced to Mn^{2+}



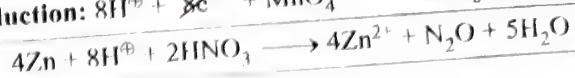
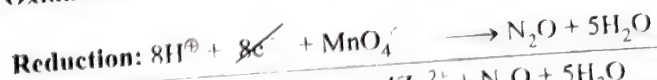
Oxidation:



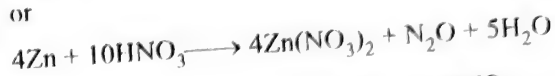
vi. Since HNO_3 is reduced to N_2O [$8e^- + 2HNO_3 \rightarrow N_2O$], so Zn must be oxidised to Zn^{2+} [$Zn \rightarrow Zn^{2+} + 2e^-$]



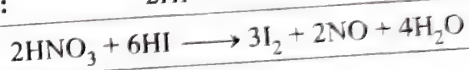
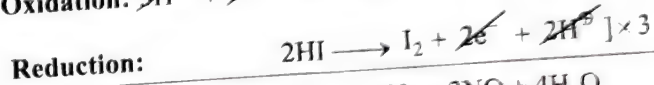
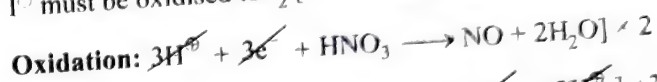
Oxidation:



or



vii. Since HNO_3 is reduced to NO [$3e^- + HNO_3 \rightarrow NO$], so I^- must be oxidised to I_2 [$2I^- \rightarrow I_2 + 2e^-$]



Single Correct Answer Type

1. Which of the following represents a redox reaction?

- (1) $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$
 (2) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{HCl}$
 (3) $\text{CuSO}_4 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}(\text{OH})_2 + \text{H}_2\text{SO}_4$
 (4) $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$

2. In the reaction



the substance oxidised is

- (1) H_2S (2) SO_2 (3) S (4) H_2O

3. In the reaction



the element which loses as well as gains electrons is

- (1) Na (2) O (3) Cl (4) None of these

4. The oxidation number of oxygen in OF_2 is

- (1) +2 (2) -2 (3) +1 (4) -1

5. An oxidation process involves

- (1) Increase in oxidation number
 (2) Decrease in oxidation number
 (3) Both decrease and increase in oxidation number
 (4) No change in oxidation number

6. Which of the following is the strongest reducing agent in aqueous medium?

- (1) Mg (2) Na (3) Li (4) Ca

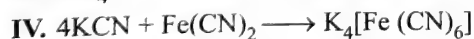
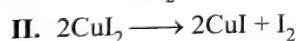
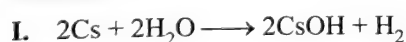
7. Which of the following is the strongest oxidising agent?

- (1) I_2 (2) F_2 (3) Cl_2 (4) Br_2

8. The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is

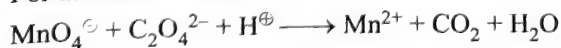
- (1) +3 (2) +2 (3) +1 (4) -1

9. Which of the following reactions do not involve oxidation-reduction?



- (1) I, II (2) I, III (3) I, III, IV (4) III, IV

10. For the redox reaction



the correct coefficients of the reactions for the balanced reaction are

MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+
(1) 2	5	16
(2) 16	5	2
(3) 5	16	2
(4) 2	16	5

11. The oxidation state of nitrogen is correctly given for

Compound **Oxidation state**

- (1) $[\text{CO}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 0
 (2) NH_2OH -2
 (3) $(\text{N}_2\text{H}_5)_2\text{SO}_4$ +2
 (4) Mg_3N_2 -3

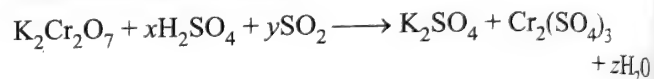
12. The oxidation state of chromium in $\text{Cr}(\text{CO})_6$ is

- (1) 0 (2) +2 (3) -2 (4) +6

13. Which of the following is not a redox reaction?

- (1) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
 (2) $\text{O}_2 + 2\text{H}_2 \longrightarrow 2\text{H}_2\text{O}$
 (3) $\text{Na} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \frac{1}{2}\text{H}_2$
 (4) $\text{MnCl}_3 \longrightarrow \text{MnCl}_2 + (1/2)\text{Cl}_2$

14. In the chemical reaction,



x , y , and z are

- (1) 1, 3, 1 (2) 4, 1, 4 (3) 3, 2, 3 (4) 2, 1, 2

15. A mole of N_2H_4 loses 10 mol of electrons to form a new compound Y . Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y ? (There is no change in the oxidation number of hydrogen.)

- (1) -1 (2) -3 (3) +3 (4) +5

16. When copper is treated with a certain concentration of nitric acid, nitric oxide and nitrogen dioxide are liberated in equal volumes according to the equation



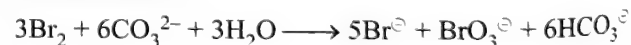
The coefficients x and y are

- (1) 2 and 3 (2) 2 and 6 (3) 1 and 3 (4) 3 and 8

17. In which of the following pairs is there the greatest difference in the oxidation numbers of the underlined elements?

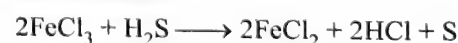
- (1) $\underline{\text{N}}\text{O}_2$ and $\underline{\text{N}}_2\text{O}_4$ (2) $\underline{\text{P}}_2\text{O}_5$ and $\underline{\text{P}}_4\text{O}_{10}$
 (3) $\underline{\text{N}}_2\text{O}$ and $\underline{\text{N}}\text{O}$ (4) $\underline{\text{S}}\text{O}_2$ and $\underline{\text{S}}\text{O}_3$

18. In the reaction



- (1) Bromine is oxidised and carbonate is reduced
 (2) Bromine is reduced and water is oxidised
 (3) Bromine is neither reduced nor oxidised
 (4) Bromine is both reduced and oxidised

19. In the reaction



- (1) FeCl_3 acts as an oxidising agent
 (2) Both H_2S and FeCl_3 are oxidised
 (3) FeCl_3 is oxidised while H_2S is reduced
 (4) H_2S acts as an oxidising agent

20. The oxidation number of cobalt in $K[Co(CO)_4]$ is
 (1) +1 (2) +3 (3) -1 (4) -3
21. Which of the following is not a disproportionation reaction?
 I. $NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$
 II. $P_4 \xrightarrow{\Delta} PH_3 + HPO_2^\ominus$
 III. $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$
 IV. $IO_3^\ominus + I^\ominus \longrightarrow I_2$
 (1) I, II (2) I, III, IV
 (3) II, IV (4) I, III
22. Which of the following represents redox reactions?
 I. $Cr_2O_7^{2-} + 2OH^\ominus \longrightarrow 2CrO_4^{2-} + H_2O$
 II. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$
 III. $2MnO_4^\ominus + 3Mn^{2+} + 4OH^\ominus \longrightarrow 5MnO_2 + 2H_2O$
 IV. $2Cu^\oplus \longrightarrow Cu + Cu^{2+}$
 (1) I, II (2) I, III, (3) III, IV (4) II, III, IV
23. In which of the following cases is the oxidation state of N atom wrongly calculated?
- | Compound | Oxidation state |
|----------------------|-----------------|
| (1) NH_4Cl | -3 |
| (2) $(N_2H_5)_2SO_4$ | +2 |
| (3) Mg_3N_2 | -3 |
| (4) NH_2OH | -1 |
24. Which of the following is not a disproportionation reaction?
 (1) $KO_2 + H_2O + CO_2 \longrightarrow KHCO_3 + O_2$
 (2) $KClO_3 \longrightarrow KClO_4 + KCl$
 (3) $PbO_2 + H_2O \longrightarrow PbO + H_2O_2$
 (4) $OHC-COOH \xrightarrow{OH^\ominus} HOH_2C-COOH + ^\ominus OOC-COO^\ominus$
25. The number of moles of $K_2Cr_2O_7$ reduced by 1 mol of Sn^{2+} ions is
 (1) 1/3 (2) 3 (3) 1/6 (4) 6
26. Which of the following is a redox reaction?
 (1) H_2SO_4 with NaOH
 (2) In atmosphere, O_3 forms O_2 by lightning
 (3) Nitrogen oxides form nitrogen and oxygen by lightning
 (4) Evaporation of H_2O
27. The oxidation state of Fe in $Fe(CO)_5$ is
 (1) 0 (2) +2 (3) -2 (4) +6
28. In which of the following pairs is there the greatest difference in the oxidation numbers of the underlined elements?
 (1) $\underline{N}O_2$ and \underline{N}_2O_4 (2) $\underline{S}O_3^{2-}$ and $\underline{S}O_4^{2-}$
 (3) $\underline{N}O_2$ and \underline{N}_2O_4 (4) \underline{S}^{2-} and $\underline{S}O_4^{2-}$
29. Which of the following is not an intermolecular redox reaction?
 (1) $MgCO_3 \longrightarrow MgO + CO_2$
 (2) $O_2 + 2H_2 \longrightarrow 2H_2O$
 (3) $K + H_2O \longrightarrow KOH + (1/2)H_2$
 (4) $MnBr_3 \longrightarrow MnBr_2 + (1/2)Br_2$
30. The number of moles of $KMnO_4$ required to oxidise 1 mol of $Fe(C_2O_4)$ in acidic medium is
 (1) 0.6 (2) 1.67 (3) 0.2 (4) 0.4
31. In the reaction
 $K + O_2 \longrightarrow KO_2$
 (1) O_2 acts as an oxidising agent
 (2) Both K and O_2 are oxidised
 (3) O_2 is oxidised while K is reduced
 (4) K acts as an oxidising agent
32. Which of the following is the best description of the behaviour of bromine in the reaction given below?
 $H_2O + Br_2 \longrightarrow HOBr + HBr$
 (1) Proton acceptor only
 (2) Both oxidised and reduced
 (3) Oxidised only
 (4) Reduced only
33. $Cr_2O_7^{2-} + X \xrightarrow{H^\oplus} Cr^{3+} + H_2O + \text{oxidised product of } X$, X in the above reaction cannot be
 (1) $C_2O_4^{2-}$ (2) Fe^{2+} (3) SO_4^{2-} (4) S^{2-}
34. The oxidation state of chromium in the final product formed in the reaction between KI and acidified potassium dichromate solution is
 (1) +4 (2) +6 (3) +2 (4) +3
35. The number of moles of $KMnO_4$ reduced by 1 mol of KI in alkaline medium is
 (1) 1 (2) 2 (3) 5 (4) 1/5
36. In the balanced chemical reaction
 $IO_3^\ominus + aI^\ominus + bH^\ominus \longrightarrow cH_2O + dI_2$
 a, b, c, and d, respectively, correspond to
 (1) 5, 6, 3, 3 (2) 5, 3, 6, 3 (3) 3, 5, 3, 6 (4) 5, 6, 5, 5
37. For the reaction
 $M^{x+} + MnO_4^\ominus \longrightarrow MO_3^\ominus + Mn^{2+} + (1/2)O_2$
 if 1 mol of MnO_4^\ominus oxidises 1.67 mol of M^{x+} to MO_3^\ominus , then the value of x in the reaction is
 (1) 5 (2) 3 (3) 2 (4) 1
38. $aK_2Cr_2O_7 + bKCl + cH_2SO_4 \longrightarrow xCrO_2Cl_2 + yKHSO_4 + zH_2O$
 The above equation balances when
 (1) $a = 2, b = 4, c = 6$ and $x = 2, y = 6, z = 3$
 (2) $a = 4, b = 2, c = 6$ and $x = 6, y = 2, z = 3$
 (3) $a = 6, b = 4, c = 2$ and $x = 6, y = 3, z = 2$
 (4) $a = 1, b = 4, c = 6$ and $x = 2, y = 6, z = 3$
39. The oxidation number of carbon in CH_2Cl_2 is
 (1) 0 (2) 2 (3) 3 (4) 5
40. Excess of KI reacts with $CuSO_4$ solution, and $Na_2S_2O_3$ solution is added to it. Which of the following statements is incorrect for the reaction?
 (1) Evolved I_2 is reduced. (2) CuI_2 is formed.
 (3) $Na_2S_2O_3$ is oxidised. (4) Cu_2I_2 is formed.

41. The oxidation number of S in H_2SO_5 is
(1) +8 (2) +6 (3) +4 (4) +2
42. The number of peroxide bonds in perxenate ion $[\text{XeO}_6]^{4-}$ is
(1) 0 (2) 2 (3) 3 (4) 1
43. The oxidation number of Pr in Pr_6O_{11} is
(1) $\frac{22}{6}$ (2) $\frac{20}{6}$ (3) 3 (4) 4
44. In which of the following is the highest oxidation state not possible?
(1) $[\text{XeO}_6]^{4-}$ (2) XeF_8 (3) OsO_4 (4) RuO_4
45. Which of the following statements is not correct about the reaction given below?

$$\text{K}_4[\text{Fe}(\text{CN})_6] \xrightarrow{\text{Oxidation}} \text{Fe}^{3+} + \text{CO}_2 + \text{NO}_3^-$$
 (1) Fe is oxidised from Fe^{2+} to Fe^{3+} .
 (2) Carbon is oxidised from C^{2+} to C^{4+} .
 (3) N is oxidised from N^{3-} to N^{5+} .
 (4) Carbon is not oxidised.
46. Which of the following is not a disproportionation reaction?
 (1) $\text{P}_4 + 5\text{OH}^- \longrightarrow \text{H}_2\text{PO}_2^- + \text{PH}_3$
 (2) $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}^-$
 (3) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 (4) $\text{PbO}_2 + \text{H}_2\text{O} \longrightarrow \text{PbO} + \text{H}_2\text{O}_2$
47. Which of the following is not an intramolecular redox reaction?
 (1) $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
 (2) $2\text{Mn}_2\text{O}_7 \longrightarrow 4\text{MnO}_2 + 3\text{O}_2$
 (3) $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
 (4) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
48. In the equation

$$\text{NO}_2^- + \text{H}_2\text{O} \longrightarrow \text{NO}_3^- + 2\text{H}^+ + n\text{e}^-$$
 n stands for
 (1) 1 (2) 2 (3) 3 (4) 4
49. Which of the following is an intermolecular redox reaction?
 (1) $2 \text{OCH} - \text{CHO} \xrightarrow{\text{OH}^-} \text{HOCH}_2 - \text{CH}_2\text{OH}$
 (2) $2\text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{Al}(\text{OC}_2\text{H}_5)_3} \text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (3) $4\text{CrO}_5 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{Cr}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} + 7\text{O}_2$
 (4) $\text{As}_2\text{S}_3 + \text{HNO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4 + \text{NO}$
50. The oxidation state of A, B, and C in a compound are +2, +5, and -2, respectively. The compound is
 (1) $\text{A}_2(\text{BC})_2$ (2) $\text{A}_2(\text{BC})_3$ (3) $\text{A}_3(\text{BC}_4)_2$ (4) $\text{A}_2(\text{BC}_4)_3$
51. The number of electrons lost in the following change is

$$\text{Fe} + \text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$$
 (1) 2 (2) 4 (3) 6 (4) 8
52. The oxidation number of Pt in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ is
 (1) +1 (2) +2 (3) +3 (4) +4
53. The oxidation number of P in $\text{Mg}_2\text{P}_2\text{O}_7$ is
 (1) +3 (2) +2 (3) +5 (4) -3
54. The oxidation number of phosphorous in PO_4^{3-} , P_4O_{10} , and $\text{P}_2\text{O}_7^{4-}$ is
 (1) +5 (2) +3 (3) -3 (4) +2
55. Which of the following leads to redox reaction?
 (1) $\text{AgNO}_3 + \text{HCl}$ (2) $\text{KOH} + \text{HCl}$
 (3) $\text{KI} + \text{Cl}_2$ (4) $\text{NH}_3 + \text{HCl}$
56. The oxidation number of S in $\text{Na}_2\text{S}_4\text{O}_6$ is
 (1) +0.5 (2) 2.5 (3) +4 (4) +6
57. The oxidation state of iodine in H_4IO_6^- is
 (1) +7 (2) -1 (3) +5 (4) +1
58. When iron is rusted, it is
 (1) Oxidised (2) Reduced
 (3) Evaporated (4) Decomposed
59. An element that never has a positive oxidation state in any of its compounds is
 (1) Boron (2) Oxygen (3) Chlorine (4) Fluorine
60. Starch iodide paper is used to test for the presence of
 (1) Iodine (2) Iodide ion
 (3) Oxidising agent (4) Reducing agent
61. Which of the following acids possesses oxidising, reducing, and complex forming properties?
 (1) HNO_3 (2) H_2SO_4 (3) HCl (4) HNO_2
62. In the reaction

$$8\text{Al} + 3\text{Fe}_3\text{O}_4 \longrightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$$
 the number of electrons transferred from the reductant to the oxidant is
 (1) 8 (2) 4 (3) 16 (4) 24
63. Which of the following examples does not represent disproportionation?
 (1) $\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
 (2) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 (3) $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 (4) $3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$
64. Which of the following statements is not correct?
 (1) The oxidation number of S in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is +6.
 (2) The oxidation number of Os in OsO_4 is +8.
 (3) The oxidation number of S in H_2SO_5 is +8.
 (4) The oxidation number of O in KO_2 is -1/2.
65. The oxidant which cannot act as a reducing agent is
 (1) SO_2 (2) NO_2 (3) CO_2 (4) ClO_2
66. The coordination number and oxidation number of Cr in $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ are, respectively,
 (1) 4 and +2 (2) 6 and +3 (3) 3 and -3 (4) 3 and 0
67. Which of the following reactions does not involve either oxidation or reduction?
 (1) $\text{VO}^{2+} \longrightarrow \text{V}_2\text{O}_3$ (2) $\text{Na} \longrightarrow \text{Na}^+$
 (3) $\text{CrO}_4^{2-} \longrightarrow \text{Cr}_2\text{O}_7^{2-}$ (4) $\text{Zn}^{2+} \longrightarrow \text{Zn}$
68. In which of the following processes is nitrogen oxidised?
 (1) $\text{NH}_4^+ \longrightarrow \text{N}_2$ (2) $\text{NO}_3^- \longrightarrow \text{NO}$
 (3) $\text{NO}_2 \longrightarrow \text{NO}_2^-$ (4) $\text{NO}_3^- \longrightarrow \text{NH}_4^+$

69. The oxidation number of C in HNC is
(1) +2 (2) -3 (3) +3 (4) 0
70. The oxidation number of Fe in $\text{Fe}_{0.94}\text{O}$ is
(1) 200 (2) 200/94 (3) 94/200 (4) None
71. The oxidation number of Fe in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is
(1) +2 (2) +1 (3) +3 (4) -2
72. The oxidation number of Cl in CaOCl_2 is
(1) -1 and +1 (2) +2 (3) -2 (4) None
73. The equivalent weight of FeC_2O_4 in the change
 $\text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + \text{CO}_2$ is
(1) M/3 (2) M/6 (3) M/2 (4) M/1
74. The oxidation state of Fe in Fe_3O_8 is
(1) 3/2 (2) 4/5 (3) 5/4 (4) 16/3
75. In which of the following compounds, the oxidation state of transition metal is zero?
(1) CrO_5 (2) Fe_3O_4 (3) FeSO_4 (4) $\text{Fe}(\text{CO})_5$
76. The oxidation state of S in $\text{H}_2\text{S}_2\text{O}_8$ is
(1) +2 (2) +4 (3) +6 (4) +7
77. Which of the following is not a disproportionation reaction?
(1) $2\text{PhCHO} \xrightarrow{\text{Al}(\text{OEt})_3} \text{PhCOOCH}_2\text{Ph}$
(2) $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array} + \text{OH}^- \longrightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COO}^- \end{array} + \begin{array}{c} \text{COO}^- \\ | \\ \text{COO}^- \end{array}$
(3) $\text{NaH} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$
(4) All
78. Which of the following is a disproportionation reaction?
(1) $\text{Cu}_2\text{O} + 2\text{H}^+ \longrightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O}$
(2) $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$
(3) $\text{CaCO}_3 + 2\text{H}^+ \longrightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$
(4) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
79. When KMnO_4 acts as an oxidising agent and ultimately from MnO_4^{2-} , MnO_2 , Mn_2O_3 , and Mn^{2+} , then the numbers of electrons transferred in each case, respectively, are
(1) 4, 3, 1, 5 (2) 1, 5, 3, 7
(3) 1, 3, 4, 5 (4) 3, 5, 7, 1
80. Which of the following is a redox reaction?
(1) $\text{NaCl} + \text{KNO}_3 \longrightarrow \text{NaNO}_3 + \text{KCl}$
(2) $\text{CaC}_2\text{O}_4 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4$
(3) $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} \longrightarrow \text{MgCl}_2 + 2\text{NH}_4\text{OH}$
(4) $\text{Zn} + 2\text{AgCN} \longrightarrow 2\text{Ag} + \text{Zn}(\text{CN})_2$
81. The oxidation states of sulphur in the anions SO_3^{2-} , $\text{S}_2\text{O}_4^{2-}$, and $\text{S}_2\text{O}_6^{2-}$ follow the order
(1) $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-}$ (2) $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$
(3) $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$ (4) $\text{S}_2\text{O}_6^{2-} < \text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-}$
82. For decolourisation of 1 mol of KMnO_4 , the moles of H_2O_2 required is
(1) 1/2 (2) 3/2 (3) 5/2 (4) 7/2
83. A metal ion M^{3+} loses three electrons; its oxidation number will be
(1) +3 (2) +6 (3) 0 (4) -3
84. To an acidic solution of an anion, a few drops of KMnO_4 solution are added. Which of the following, if present, will not decolourise the KMnO_4 solution?
(1) CO_3^{2-} (2) NO_2^- (3) S^{2-} (4) Cl^-
85. The number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ reduced by 1 mol of Sn^{2+} is
(1) 1/6 (2) 1/3 (3) 2/3 (4) 1
86. Which of the following is not a reducing agent?
(1) SO_2 (2) H_2O_2 (3) CO_2 (4) NO_2
87. The oxidation state of chromium in $[\text{Cr}(\text{PPh}_3)_3(\text{CO})_3]$ is
(1) +3 (2) +8 (3) 0 (4) +5
88. The values of x and y in the following redox reaction.
 $x\text{Cl}_2 + 6\text{OH}^- \longrightarrow \text{ClO}_3^- + y\text{Cl}^- + 3\text{H}_2\text{O}$ are
(1) x = 2, y = 4 (2) x = 5, y = 3
(3) x = 3, y = 5 (4) x = 4, y = 2
89. Which gas is evolved when PbO_2 is treated with conc HNO_3 ?
(1) NO_2 (2) O_2 (3) N_2 (4) N_2O
90. The equivalent mass of oxidising agent in the following reaction is
 $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + 2\text{H}_2\text{O}$
(1) 32 (2) 64 (3) 16 (4) 8
91. In alkaline medium, ClO_2 oxidises H_2O_2 to O_2 and is itself reduced to Cl^- . How many moles of H_2O_2 are oxidised by 1 mol of ClO_2 ?
(1) 1 (2) 3/2 (3) 5/2 (4) 7/2

Multiple Correct Answers Type

1. Which of the following compounds can be oxidised further with a strong oxidising agent?
(1) CrO_3 (2) Al_2O_3 (3) SO_2 (4) MnO_3
2. Which of the following statements is/are correct?
(1) The oxidation state of H in LiAlH_4 is -1.
(2) The oxidation state of H in LiAlH_4 is +1.
(3) The reaction of hydrogen in that oxidation state with H_2O is
 $\text{H}^- + \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{OH}^-$
(4) The reaction of hydrogen in that oxidation state with H_2O is
 $\text{H}^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+$
3. Which of the following statements is/are correct?
(1) The oxidation states of N in NH_3 , HN_3 , and N_2H_4 are -3, -1/3, and -2, respectively.
(2) The oxidation states of N in NO_2 , N_2O_4 , and N_2O are +4, +4, and +3, respectively.
(3) The oxidation states of N in NH_2OH , N_2 , and N_2O are -1, +2, and +5, respectively.
(4) The oxidation states of N in N_2O are -3, respectively.

moles	4
ant	5
q.	2/5

4. Which of the following reactions should be balanced in basic medium?

- (1) $\text{NH}_3 + \text{MnO}_4^- \longrightarrow \text{MnO}_2 + \text{NO}_2$
- (2) $\text{Cr}(\text{OH})_2 + \text{I}_2 \longrightarrow \text{Cr}(\text{OH})_3 + 2\text{I}^-$
- (3) $\text{HNO}_3 + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{NO}_2$
- (4) $\text{H}_2\text{O}_2 + \text{Fe}^{3+} \longrightarrow \text{O}_2 + \text{Fe}^{2+}$

5. Which of the following reactions is not a redox reaction?

- (1) $\text{H}_2\text{O}_2 + \text{KOH} \longrightarrow \text{KHO}_2 + \text{H}_2\text{O}$
- (2) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
- (3) $\text{Ca}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
- (4) $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$

6. No reaction occurs in which of the following equations?

- (1) $\text{I}^- + \text{Fe}^{2+} \longrightarrow$
- (2) $\text{F}_2 + 2\text{NaCl} \longrightarrow$
- (3) $\text{Cl}_2 + 2\text{NaF} \longrightarrow$
- (4) $\text{I}_2 + 2\text{NaBr} \longrightarrow$

7. Which of the following statements is/are correct?

- (1) In the reaction $\text{H}_2\text{O}_2 + \text{I}_2 \longrightarrow \text{I}^- + ?$ the missing product is O_2 .
- (2) In the above reaction (a), the missing product is H_2O .
- (3) In the reaction $\text{H}_2\text{O}_2 + \text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + ?$, the missing product is O_2 .
- (4) In the above reaction (c), the missing products is H_2O .

8. Which of the following statements is/are correct?

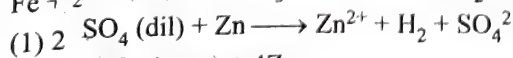
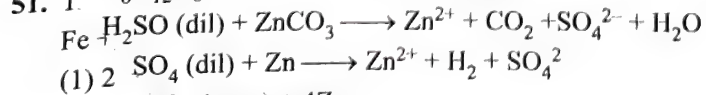
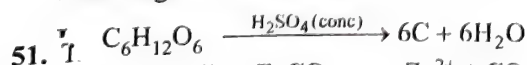
- (1) In the reaction $\text{MnO}_4^{2-} + \text{H}^+ \longrightarrow \text{Mn}^{2+} + ?$ the missing product is MnO_4^- .
- (2) In the above reaction (a), the missing product is MnO_2 .
- (3) In the reaction $\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{NO} + ?$ the missing product is NO_3^- .
- (4) In the above reaction (3), the missing product is NO_2^- .

9. Which of the following statements is/are correct?

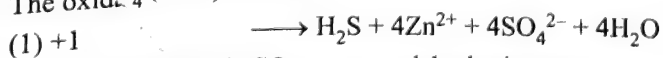
In the reaction $x\text{Cu}_3\text{P} + y\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4 + \text{Cr}^{3+}$

- (1) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is also oxidised to PO_4^{3-} .
- (2) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is reduced to H_3PO_4 .
- (3) In the conversion of Cu_3P to Cu^{2+} and H_3PO_4 , 11 electrons are involved.
- (4) The value of x is 6.

10. Which of the following statements is/are correct about the following reactions?



52. The oxidation of Zn by $\text{H}_2\text{SO}_4(\text{conc}) + 4\text{Zn}$



(1) +1

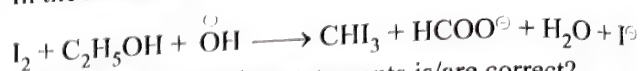
53. The oxidation of I , H_2SO_4 acts as a dehydrating agent.

(1) +3 (2) H_2SO_4 acts as an acid.

(3) In reaction (III), H_2SO_4 acts both as an acid and an oxidising agent.

(4) In reaction (IV), H_2SO_4 acts as an oxidising agent.

11. In the reaction



which of the following statements is/are correct?

(1) The coefficients of OH^- and I^- in the given balanced equation are, respectively, 6 and 5.

(2) The coefficients of OH^- and I^- in the given balanced equation are, respectively, 5 and 6.

(3) $\text{C}_2\text{H}_5\text{OH}$ is oxidised to CHI_3 and HCOO^- .

(4) The number of electrons in the conversion of $\text{C}_2\text{H}_5\text{OH}$ to CHI_3 and HCOO^- is 8.

12. Which of the following statements is/are correct?

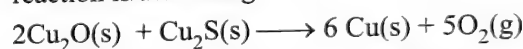
(1) PbO_2 reacts with HCl to evolve Cl_2 gas.

(2) PbO_2 reacts with HNO_3 to form O_2 gas.

(3) Pb_3O_4 reacts with HCl to evolve Cl_2 gas.

(4) Pb_3O_4 reacts with HNO_3 to form PbO_2 , but O_2 is not liberated.

13. Which of the following statements about the following reaction is/are wrong?



(1) Both Cu_2O and Cu_2S are reduced.

(2) Only Cu_2S is reduced.

(3) Cu_2S is the oxidant.

(4) Only Cu_2O is reduced.

14. The oxidation number of Cr is +6 in

(1) FeCr_2O_4

(2) KCrO_3Cl

(3) CrO_5

(4) $[\text{Cr}(\text{OH})_4]^-$

15. The oxidation number of carbon is zero in

(1) HCHO

(2) CH_2Cl_2

(3) $\text{C}_6\text{H}_{12}\text{O}_6$

(4) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

16. Which of the following has/have been arranged in order of decreasing oxidation number of sulphur?

(1) $\text{H}_2\text{S}_2\text{O}_7 > \text{Na}_2\text{S}_4\text{O}_6 > \text{Na}_2\text{S}_2\text{O}_3 > \text{S}_8$

(2) $\text{SO}^{2+} > \text{SO}_4^{2-} > \text{SO}_3^{2-} > \text{HSO}_4^-$

(3) $\text{H}_2\text{SO}_5 > \text{H}_2\text{SO}_3 > \text{SO}_2 > \text{H}_2\text{S}$

(4) $\text{H}_2\text{SO}_4 > \text{SO}_2 > \text{H}_2\text{S} > \text{H}_2\text{S}_2\text{O}_8$

17. The oxidation number of carboxylic carbon atom in CH_3COOH is

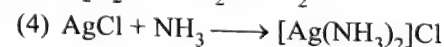
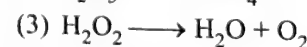
(1) +2

(2) +4

(3) +1

(4) +3

18. Which of the following is/are autoredox reactions?



19. Which of the following is/are disproportionation reactions?

- (1) $2\text{O}_3 \longrightarrow 3\text{O}_2$
- (2) $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
- (3) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
- (4) $2\text{KO}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{KOH} + 3\text{O}_2$

20. For the reaction $\text{KO}_2 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{KHCO}_3 + \text{O}_2$, the mechanism of reaction suggests

- (1) Acid-base reaction (2) Disproportionation reaction
- (3) Hydrolysis (4) Redox change

21. Which of the following can be used both as an oxidant and a reductant?

- (1) HNO_2 (2) SO_2 (3) O_2 (4) CO

22. Which molecules represented by the bold atoms are in their highest oxidation state?

- (1) $\text{H}_2\text{S}_2\text{O}_8$ (2) P_4O_{10} (3) F_2O (4) Mn_2O_7

23. Which molecules represented by the bold atoms are in their lowest oxidation state?

- (1) F_2O (2) H_2S (3) PH_3 (4) N_2H_4

24. Which of the following statements is/are correct about $\text{CH}_2=\text{CCl}_2$

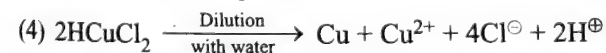
- (1) Both carbons are in +2 oxidation state.
- (2) Both carbons are in -2 oxidation state.
- (3) The first carbon has +2 and the second has -2 oxidation states.
- (4) The average oxidation number of carbon is zero.

25. Which of the following statements about tailing of Hg is/are correct?

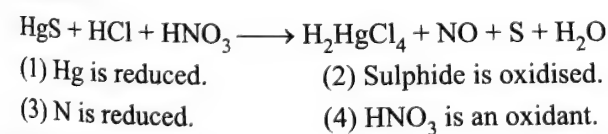
- (1) It is due to Hg_2O . (2) It is due to HgO .
- (3) It is removed by H_2O_2 . (4) It is removed by O_3 .

26. Which of the following is/are disproportionation redox changes?

- (1) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
- (2) $5\text{H}_2\text{O}_2 + 2\text{ClO}_2 + 2\text{OH}^- \longrightarrow 2\text{Cl}^- + 5\text{O}_2 + 6\text{H}_2\text{O}$
- (3) $3\text{ClO}^- \longrightarrow \text{ClO}_3^- + \text{Cl}^-$



27. Which of the following statements about the reaction is/are correct?



- (1) Hg is reduced. (2) Sulphide is oxidised.
- (3) N is reduced. (4) HNO_3 is an oxidant.

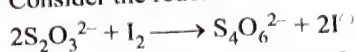
28. Which of the following substances undergo(es) disproportionation reactions under basic medium?

- (1) F_2 (2) P_4 (3) S_8 (4) Br_2

29. Which of the following represent redox reactions?

- (1) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
- (2) $\text{SO}_3^{2-} + \text{H}_2\text{O} + \text{I}_2 \longrightarrow \text{SO}_4^{2-} + 2\text{I}^- + 2\text{H}^+$
- (3) $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \longrightarrow \text{Ca}(\text{OCl})_2 + \text{CaCl}_2$
- (4) $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$

30. Consider the redox reaction



- (1) $\text{S}_2\text{O}_3^{2-}$ gets reduced to $\text{S}_4\text{O}_6^{2-}$.
- (2) $\text{S}_2\text{O}_3^{2-}$ gets reduced to $\text{S}_4\text{O}_6^{2-}$.
- (3) I_2 gets reduced to I^- .
- (4) I_2 gets oxidised to I^- .

31. Which of the following compounds acts both as an oxidising as well as a reducing agent?

- (1) HNO_2 (2) H_2O_2 (3) H_2S (4) SO_2

32. Which of the following reactions does not involve oxidation-reduction?

- (1) $2\text{Rb} + 2\text{H}_2\text{O} \longrightarrow 2\text{RbOH} + \text{H}_2$
- (2) $2\text{CuI}_2 \longrightarrow 2\text{CuI} + \text{I}_2$
- (3) $\text{NH}_4\text{Cl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O}$
- (4) $4\text{KCN} + \text{Fe}(\text{CN})_2 \longrightarrow \text{K}_4[\text{Fe}(\text{CN})_6]$

Linked Comprehension Type

Paragraph 1

Consider the following unbalanced redox reaction:



The oxidation number of X is -2, and neither X nor water is involved in the redox process.

1. The element(s) undergoing oxidation is/are

- (1) A (2) B
- (3) Y (4) B or Y or both

2. The possible oxidation states of B and Y in BY are, respectively,

- (1) +1, -1 (2) +2, -2
- (3) +3, -3 (4) All of these

3. If the above reaction is balanced with smallest whole number coefficients, the sum of the stoichiometric coefficients of all the compounds is

- (1) 9 (2) 8 (3) 7 (4) 6

Paragraph 2

Oxidation reaction involves loss of electrons, and reduction reaction involves gain of electrons. The reaction in which a species disproportionates into two oxidation states (lower and higher) is called disproportionation reaction.

4. Which of the following statements is wrong?

- (1) An acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper on being exposed to SO_2 turns green.
- (2) Mercuric chloride and stannous chloride cannot exist at such.
- (3) Iron turning on addition to CuSO_4 solution decolourises the blue colour.
- (4) $[\text{CuI}_4]^{2-}$ is formed but $[\text{CuCl}_4]^{2-}$ is not.

5. Which of the following statements is wrong?

- (1) Acidified KMnO_4 solution decolourises of sodium oxalate.
- (2) In the reaction between Br_2 and C_6H_6 , C_6H_6 is a reducing agent and CsI is a reducing agent.

$\frac{2}{5}$

- (3) In the reaction $2K_2S_2O_3 + I_2 \longrightarrow 2KI + K_2S_4O_6$, the change in the oxidation number of S is 0.5.
- (4) C has the same oxidation number in both CH_4 and CO_2 .
6. Which of the following statements is correct?
- An element in the lowest oxidation state acts only as a reducing agent.
 - An element in the highest oxidation state acts only as a reducing agent.
 - The oxidation number of V in $Rb_4K(HV_{10}O_{28})$ is +4.
 - The oxidation number and valency of Hg in calomel is +1.
7. Which of the following statements is wrong?
- The algebraic sum of the oxidation numbers of all atoms in an ion is zero.
 - The oxidation number is an arbitrary number. It can have positive, negative, zero, or fractional values.
 - When a negative ion changes to neutral species, the process is oxidation.
 - The oxidation number of phosphorous can vary from -3 to +5.
8. Which of the following is not a disproportionation reaction?
- $\bar{O}H + Br_2 \longrightarrow Br^- + BrO_3^-$
 - $Cu_2O + 2H^+ \longrightarrow Cu + Cu^{2+} + H_2O$
 - $(CN)^- \longrightarrow CO_3^{2-} + NO_3^-$
 - $(CN)_2 + 2\bar{O}H \longrightarrow CN^- + CNO^- + H_2O$

Paragraph 3

The valency of carbon is generally 4, but its oxidation state may be -4, -2, 0, +2, -1, etc. In the compounds containing C, H, and O, the oxidation number of C is calculated as

$$\text{Oxidation number of C} = \frac{2n_O - n_H}{n_C}$$

where n_O , n_H , and n_C are the number of oxygen, hydrogen, and carbon atoms, respectively.

9. The oxidation state of C in diamond is
- 0
 - +1
 - 1
 - +2
10. In which of the following compounds is the valency of C two?
- Ketenes
 - Alkenes
 - Allenes
 - Carbenes
11. In which of the following compounds is the oxidation state of carbon is zero?
- CH_4
 - CH_3OH
 - $HCOOH$
 - $C_6H_{12}O_6$
- In which of the following compounds is the oxidation state of C highest?
- $FeHCOOH$
 - $HCHO$
 - $2 \cdot \bar{I}_3OH$
 - CH_4
52. The oxⁿ of the following compounds is the oxidation state
- +1
 - CO_2
 - 1
 - All
53. The oxidatⁿ of the following compounds is the oxidation state
- +3
 - 1
 - 2
 - All

14. Match the following:

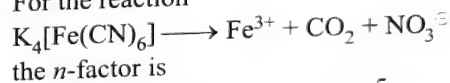
Reaction	Process
a. $CH_3 \longrightarrow CH_3OH$	p. Neither oxidation nor reduction
b. $CH_2Cl_2 \longrightarrow CH_2=O$	q. Oxidation
c. $H_2C=CH_2 \longrightarrow H_3C-CH_3$	r. Reduction
d. $HC \equiv CH \longrightarrow CH_3CH=O$	

Paragraph 4

Redox equations are balanced either by ion-electron method or by oxidation number method. Both methods lead to the correct form of the balanced equation. The ion electron method has two advantages. So some chemists prefer to use the ion-electron method for redox reactions carried out in dilute aqueous solutions, where free ions have more or less independent existence.

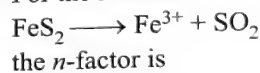
The oxidation state method for redox reactions is mostly used for solid chemicals or for reactions in concentrated acid media.

15. For the reaction



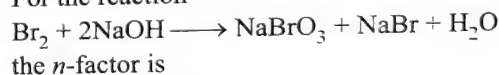
- 1
- 11
- $\frac{5}{3}$
- 61

16. For the reaction



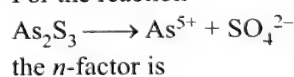
- 1
- 11
- 28
- 61

17. For the reaction



- 11
- 28
- 61
- $\frac{5}{3}$

18. For the reaction



- 11
- 28
- 61
- $\frac{5}{3}$

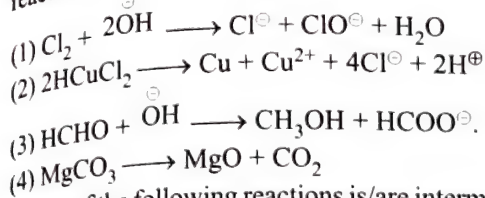
Paragraph 5

Certain materials such as turpentine oil, unsaturated organic compounds, phosphorous, metals such as Zn, and Pb, etc., can absorb O_2 from air in the presence of H_2O , which is converted to H_2O_2 . This is called autoxidation. Intermolecular redox reactions are those in which one molecule is oxidised and the other is reduced. Intramolecular redox reactions are those in which one atom of a molecule is oxidised and the other atom is reduced.

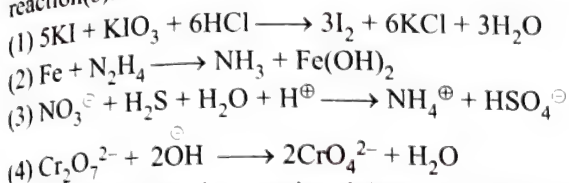
19. Which of the following reactions is/are intramolecular redox reaction(s)?

- $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$
- $K_3[Fe(CN)_6] + 30H_2O \longrightarrow Fe^{3+} + 6CO_2 + 6NO_3^- + 60H^+ + 60e^-$
- $2HgO \longrightarrow 2Hg + O_2$
- $PhCHO \xrightarrow{NaOH} PhCH_2OH + PhCOONa$

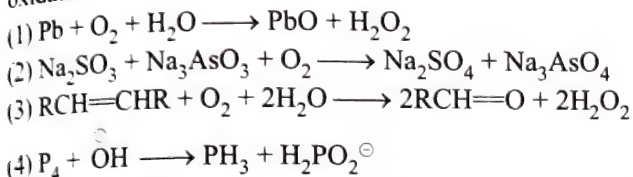
20. Which of the following reactions is/are disproportionation reaction(s)?



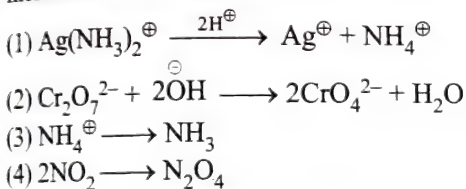
21. Which of the following reactions is/are intermolecular redox reaction(s)?



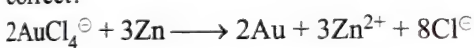
22. Which of the following reactions is/are auto redox or induced oxidation reaction(s)?



23. Which of the following reactions is/are none of the reactions mentioned in the question?

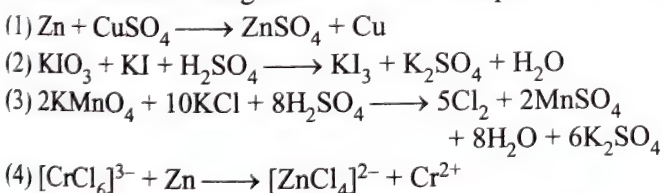


24. Which of the following statements about the reaction is/are correct?



- (1) AuCl_4^- is reduced to Au.
 (2) Zn is oxidised to Zn^{2+} .
 (3) Cl^- is a spectator ion.
 (4) It is an intermolecular redox reaction.

25. Which of the following reactions has/have spectator ions?



Matrix Match Type

1. Match the reactions given in column I with the number of electrons lost or gained in column II.

Column I		Column II
Reaction		Number of electrons lost or gained
a. $\text{Mn}(\text{OH})_2 + \text{H}_2\text{O}_2 \longrightarrow \text{MnO}_2$	p.	8
b. $\text{AlCl}_3 + 3\text{K} \longrightarrow \text{Al} + 3\text{KCl}$	q.	2
c. $3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$	r.	3
d. $\text{H}_2\text{S} + \text{NO}_3^- \longrightarrow \text{S} + \text{NO}$	s.	6

2. Match the reactions given in column I with average oxidation numbers given in column II.

Column I		Column II
Reaction		Average oxidation number of Fe
a. $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$ (Ferri-ferrocyanide) (Prussian blue)	p.	$\frac{12}{5}$
b. $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (Ferro-ferrocyanide)	q.	2
c. $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ (Ferro-ferri cyanide) (Turnbull's blue)	r.	$\frac{18}{7}$
d. $\text{Fe}[\text{Fe}(\text{CN})_6]$ (Ferri-ferricyanide)	s.	1
e. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ (Sodium nitroprusside)	t.	3
f. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$	u.	$\frac{8}{3}$
g. Fe_3O_4		

3. Match the reactions given in column I with their respective oxidant/reductant given in column II.

Column I		Column II
Reaction and substance acting as oxidant or reductant		Oxidant and reductant
a. $3\text{I}_2 + 6\text{NaOH} \longrightarrow \text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$ (I_2 acts as)	p.	None act as oxidant or reductant
b. $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{NaCl}$ BaCl_2 acts as	q.	Reductant
c. $\text{AlCl}_3 + 3\text{Na} \longrightarrow 3\text{NaCl} + \text{Al}$ AlCl_3 acts as	r.	Both act as oxidant and reductant
d. $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + \text{H}_2\text{O}$ H_2S acts as	s.	Oxidant

4. Match the reactions in column I with the molar ratio of their respective oxidants and reductant given in column II.

Column I		Column II
Reaction		Ratio of moles of oxidant to reductant
a. $\text{H}^+ + \text{U}(\text{SO}_4)_2 + \text{KMnO}_4 \longrightarrow \text{UO}_2\text{SO}_4 + \text{MnSO}_4$	p.	$\frac{1}{3}$
b. $\text{CrI}_3 + \text{Cl}_2 + \text{OH}^- \longrightarrow \text{CrO}_4^{2-} + \text{IO}_4^- + \text{Cl}^-$	q.	$\frac{2}{5}$

c.	$\text{HAsO}_3^{2-} + \text{BrO}_3^- + \text{H}^+ \longrightarrow \text{H}_3\text{AsO}_4 + \text{Br}^-$	r.	1
d.	$\text{O}_2 + \text{NH}_3 \longrightarrow \text{NO} + \text{H}_2\text{O}$	s.	$\frac{27}{2}$
e.	$\text{Sb}_2\text{O}_3 + \text{IO}_3^- + \text{H}^+ \longrightarrow \text{HSb(OH)}_6 + \text{ICl}$	t.	3
f.	$\text{WO}_3 + \text{SnCl}_2 + \text{H}^+ \longrightarrow \text{W}_3\text{O}_8 + \text{SnCl}_6^{2-}$	u.	$\frac{5}{4}$

5. Match the reactions in column I with the molar ratio of their respective reductant and oxidant given in column II.

	Column I		Column II
	Reaction		Ratio of moles of reductant to oxidant
a.	$\text{Bi}_2\text{O}_3 + \text{ClO}^- + \text{OH}^- \longrightarrow \text{BiO}_3^- + \text{Cl}^-$	p.	4
b.	$\text{MnO}_2 + \text{PbO}_2 + \text{H}^+ \longrightarrow \text{MnO}_4^- + \text{Pb}^{2+}$	q.	2
c.	$\text{TeO}_3^{2-} + \text{I}^- + \text{H}^+ \longrightarrow \text{Te} + \text{I}_2$	r.	$\frac{1}{2}$
d.	$[\text{Fe(CN)}_6]^{3-} + \text{Cr}_2\text{O}_3 + \text{OH}^- \longrightarrow [\text{Fe(CN)}_6]^{4-} + \text{CrO}_4^{2-}$	s.	$\frac{2}{5}$
e.	$\text{CoCl}_2 + \text{Na}_2\text{O}_2 + \text{OH}^- \longrightarrow \text{Co(OH)}_3$	t.	$\frac{1}{6}$

6. Match the reactions in column I with their respective products in column II.

	Column I		Column II
	Reaction of different elements with HNO_3		Product
a.	Metals such as Cu, Ag, Hg, Pb, and Zn reduce conc HNO_3 to give	p.	Metal nitrates and NO
b.	Metals in (a), except Zn, with dil HNO_3 give	q.	Metal nitrates and NO_2
c.	More active metals such as Zn, Fe, and Sn reduce dil HNO_3 and give	r.	Metal nitrates and NH_2OH or NH_4NO_3
d.	Metals in (c) with very dil HNO_3 give	s.	Metal nitrates and N_2O
e.	Moderately conc HNO_3 with Fe gives	t.	Rendered passive
f.	Fe, Al, Co, Ni, and Cr with conc HNO_3 give	u.	Ferric nitrates and NO_2
g.	Sn with conc HNO_3 gives	v.	Metal nitrates and H_2

h.	Mg, Mn, and Ca with dil HNO_3 give	w.	H_2SnO_3 and NO_2
i.	Noble metals, Au and Pt, with aqua regia (conc HCl : conc $\text{HNO}_3 = 3 : 1$) give	x.	Complex ions such as AuCl_4^- and PtCl_6^{2-} and NO

7. Match the reactions in column I with their respective products and number of electrons given in column II.

	Column I		Column II
	Reaction		Product and number of electrons
a.	$\text{S}_2\text{O}_3^{2-} + \text{H}^+ \longrightarrow$	p.	$2\text{HSO}_4^- + 8e^-$
b.	$\text{S}_2\text{O}_3^{2-} + \text{OH}^- \longrightarrow$	q.	$\text{S}_4\text{O}_6^{2-} + 2e^-$
c.	$\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \xrightarrow{\text{Neutral medium}}$	r.	$2\text{SO}_4^{2-} + 8e^-$
d.	$xe^- + \text{MnO}_4^- + \text{H}^+ \longrightarrow$	s.	$3e^-$ and MnO_2
e.	$xe^- + \text{MnO}_4^- \xrightarrow{\text{Strong basic medium}}$	t.	$5e^-$ and Mn^{2+}
f.	$xe^- + \text{MnO}_4^- \xrightarrow{\text{Mild basic or neutral medium}}$	s.	$1e^-$ and MnO_4^{2-}

8. Match the reactions in column I with the coefficients x and y given in column II.

	Column I		Column II
	Reaction		The coefficients of x and y are
a.	$x\text{Cu} + y\text{HNO}_3 \longrightarrow \text{Cu(NO}_3)_2 + \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$	p.	2 and 6
b.	$x\text{KI} + y\text{BaCrO}_4 \xrightarrow{\text{H}^+} \text{I}_2 + \text{CrCl}_3$	q.	6 and 2
c.	$x\text{As}_2\text{S}_3 + y\text{NO}_3^- \longrightarrow \text{AsO}_4^{3-} + \text{NO} + \text{SO}_4^{2-}$	r.	3 and 28
d.	$4\text{P} + 3\text{OH}^- + 3\text{H}_2\text{O} \longrightarrow x\text{PH}_3 + y\text{H}_2\text{PO}_2^-$	s.	1 and 3
e.	$x\text{KI} + y\text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{H}_2\text{S} + \text{K}_2\text{SO}_4$	t.	8 and 5

9. Match the reactions in column I with their respective characteristics given in column II.

	Column I		Column II
	Name and reaction		Characteristics
a.	$\text{P} \longrightarrow \text{PH}_3 + \text{H}_2\text{PO}_2^-$	p.	Fractional oxidation number
b.	C_3O_2	q.	Redox reaction
c.	CH_2Cl_2	r.	Natural redox reaction

d. $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$	s. Zero oxidation number
e. Photosynthesis	t. Disproportionation
	u. Auto-redox

10. Match the processes in column I with their respective names in column II.

Column I Process	Column II Name of reaction
a. Burning of gasoline and human respiration	p. Physical change
b. Preparation of metals from their ores and production by lightning of nitrogen oxides from nitrogen and oxygen in the atmosphere.	q. Neutralisation reaction
c. Evaporation of water and production by lightning of O_3 from O_2	r. Redox reaction
d. Reaction of oxalic acid with NaOH	s. Intramolecular redox reaction
e. $2\text{Mn}_2\text{O}_7 \longrightarrow 4\text{MnO}_2 + 3\text{O}_2$	t. Intermolecular redox reaction
f. $\text{Fe} + \text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + \text{Fe}(\text{OH})_2$	

Numerical Value Type

1. Among the following, what is the total number of compounds having +3 oxidation state of the underlined elements?

- a. $\text{K}_4\text{P}_2\text{O}_7$ b. NaAuCl_4 c. $\text{Rb}_4\text{Na}[\text{HV}_{10}\text{O}_{28}]$
 d. ICl e. Ba_2XeO_6 f. OF_2
 g. $\text{Ca}(\text{ClO}_2)_2$ h. NO_2^-

2. Among the compounds given in question 1, what is the total number of compounds having +5 oxidation state of the underlined elements?

3. Among the following, what is the total number of compounds having zero oxidation state of the underlined elements?

- a. SO_3^{2-} b. H_2CO c. CH_2Cl_2 d. $\text{Na}_2\text{Cr}_2\text{O}_7$
 e. O_3

4. Among the compounds given in question 3, what is the sum of the oxidation states of all underlined elements?

5. Among the following elements, what is the total number of elements having the lowest oxidation state of zero?

- a. Ta b. Te c. Tc d. Ti e. Tl

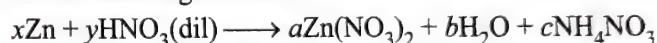
6. Among the following, what is the total number of species which are very good oxidising agents?

- a. F_2 b. F^\ominus c. Na d. Na^\oplus
 e. MnO_4^\ominus f. I^\ominus g. Cl^\ominus h. Ce^{4+}
 i. $\text{Cr}_2\text{O}_7^{2-}$ j. CrO_4^{2-} k. HNO_3 l. Fe^{2+}

7. Among the species given in Q. 6, what is the total number of species which are very good reducing agents?

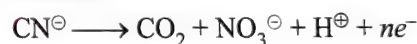
8. Among the species given in Q. 6, what is the total number of species which are neither oxidising nor reducing agents?

9. In the following reaction



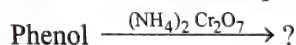
What is the sum of the coefficients ($a + b + c$)?

10. CN^\ominus ion is oxidised by a powerful oxidising agent to NO_3^\ominus and CO_2 or CO_3^{2-} depending on the acidity of the reaction mixture.



What is the number (n) of electrons involved in the process, divided by 10?

11. What is the n -factor for the phenol in the following reaction?

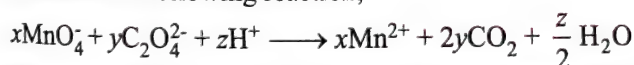


Archives

JEE MAIN

Single Correct Answer Type

1. Consider the following reaction,



The values of x , y , and z in the reaction are, respectively

- (1) 5, 2, and 16 (2) 2, 5, and 8
 (3) 2, 5, and 16 (4) 5, 2, and 8

(JEE Main 2013)

JEE ADVANCED

Single Correct Answer Type

1. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

- (1) II, III in haematite and III in magnetite
 (2) II, III in haematite and II in magnetite
 (3) II in haematite and II, III in magnetite
 (4) III in haematite and II, III in magnetite

(IIT-JEE 2011)

Multiple Correct Answers Type

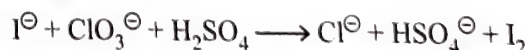
1. In which of the following reactions H_2O_2 acts as a reducing agent?

- A. $\text{H}_2\text{O}_2 + 2\text{H}^\oplus + 2e^- \longrightarrow 2\text{H}_2\text{O}$
 B. $\text{H}_2\text{O}_2 - 2e^- \longrightarrow \text{O}_2 + 2\text{H}^\oplus$
 C. $\text{H}_2\text{O}_2 + 2e^- \longrightarrow 2\text{OH}^\ominus$
 D. $\text{H}_2\text{O}_2 + 2\text{OH}^\ominus - 2e^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O}$

- (1) A, C (2) B, D (3) A, B (4) C, D

(JEE Advanced 2014)

2. For the reaction



The correct statement(s) in the balanced equation is/are:

- (1) Stoichiometric coefficient of HSO_4^\ominus is 6.
 (2) Iodide is oxidized.
 (3) Sulphur is reduced.
 (4) H_2O is one of the products.

(JEE Advanced 2014)

Numerical Value Type

1. The difference in the oxidation numbers of two types of sulphur atoms in $\text{Na}_2\text{S}_4\text{O}_6$ is (IIT-JEE 2011)

Answers Key**EXERCISES****Single Correct Answer Type**

1. (4) 2. (1) 3. (3) 4. (1) 5. (1)
 6. (3) 7. (2) 8. (3) 9. (4) 10. (1)
 11. (4) 12. (1) 13. (1) 14. (1) 15. (3)
 16. (2) 17. (4) 18. (4) 19. (1) 20. (3)
 21. (2) 22. (4) 23. (2) 24. (3) 25. (1)
 26. (3) 27. (1) 28. (4) 29. (1) 30. (1)
 31. (1) 32. (2) 33. (3) 34. (4) 35. (2)
 36. (1) 37. (3) 38. (4) 39. (1) 40. (2)
 41. (2) 42. (1) 43. (1) 44. (2) 45. (4)
 46. (4) 47. (4) 48. (2) 49. (4) 50. (3)
 51. (4) 52. (2) 53. (3) 54. (1) 55. (3)
 56. (2) 57. (1) 58. (1) 59. (4) 60. (3)
 61. (4) 62. (4) 63. (1) 64. (3) 65. (3)
 66. (2) 67. (3) 68. (1) 69. (1) 70. (2)
 71. (1) 72. (1) 73. (1) 74. (4) 75. (4)
 76. (3) 77. (3) 78. (1) 79. (3) 80. (4)
 81. (1) 82. (3) 83. (2) 84. (1) 85. (3)
 86. (3) 87. (3) 88. (3) 89. (2) 90. (3)
 91. (3)

Multiple Correct Answers Type

1. (3, 4) 2. (1, 3) 3. (1, 2, 3, 4)
 4. (1, 2) 5. (1, 2, 3) 6. (1, 3, 4)
 7. (1, 4) 8. (1, 3) 9. (1, 3, 4)
 10. (1, 2, 3, 4) 11. (1, 3, 4) 12. (1, 2, 3, 4)
 13. (2, 3, 4) 14. (2, 3) 15. (1, 2, 3, 4)
 16. (1, 3) 17. (4) 18. (1, 2, 3)
 19. (1, 2, 3, 4) 20. (1, 2, 3, 4) 21. (1, 2, 3, 4)
 22. (1, 2, 4) 23. (2, 3) 24. (1, 2, 4)
 25. (1, 3) 26. (3, 4) 27. (2, 3, 4)
 28. (2, 3, 4) 29. (2, 3, 4) 30. (2, 3)
 31. (1, 2, 4) 32. (3, 4)

Linked Comprehension Type

1. (4) 2. (4) 3. (2) 4. (4) 5. (4)
 6. (1) 7. (1) 8. (3) 9. (1) 10. (4)

11. (4) 12. (1) 13. (3)

14. (a \rightarrow q; b \rightarrow p; c \rightarrow r; d \rightarrow p)

15. (4) 16. (2) 17. (4) 18. (2) 19. (1, 3)

20. (1, 2, 3) 21. (1, 2, 3)

22. (1, 2, 3, 4) 23. (1, 2, 3, 4)

24. (1, 2, 3, 4) 25. (1, 2, 3, 4)

Matrix Match Type

Q.No.	a	b	c	d	e	f	g	h	i
1.	q	r	p	s	—	—	—	—	—
2.	r	q	p	t	q	s	u	—	—
3.	r	p	s	q	—	—	—	—	—
4.	q	s	p	u	r	t	—	—	—
5.	r	s	p	t	q	—	—	—	—
6.	q	p	s	r	u	t	w	v	x
7.	q	r	p	t	u	s	—	—	—
8.	p	q	r	s	t	—	—	—	—
9.	t, u	p	s	q	r	—	—	—	—
10.	r, t	r, t	p	q	s	r, t	—	—	—

Numerical Value Type

1. (2) 2. (2) 3. (3) 4. (10) 5. (4)
 6. (6) 7. (3) 8. (3) 9. (3) 10. (3)
 11. (4)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (3)

JEE Advanced**Single Correct Answer Type**

1. (4)

Multiple Correct Answers Type

1. (2) 2. (1, 2, 4)

Numerical Value Type

1. (5)

OVERVIEW

1. $\text{Eq (or) g Eq} = \frac{W}{Ew}$ $\left(\begin{array}{l} w = \text{weight of reactant} \\ Ew = \text{Equivalent weight} \\ \text{of that reactant} \end{array} \right)$
2. $\text{mEq} = \frac{W}{Ew} \times 1000$
3. $\text{Eq} = N \times V(\text{L})$
4. $\text{mEq} = N \times V(\text{mL})$
5. $\text{Moles} = M \times V(\text{L})$
6. $\text{Mmol} = M \times V(\text{mL})$
7. $Ew (\text{equivalent weight}) = \frac{Mw}{n}$ $\left(\begin{array}{l} Mw = \text{Molecular weight} \\ n = n\text{-factor or valency} \\ \text{factor} \end{array} \right)$

8. $\text{Strength} = \text{moles} \times Mw \text{ or } \text{Eq} \times Ew (\text{g L}^{-1})$

9. $N = n \times M$

10. Equivalent(eq) of a gas, if volume is given:

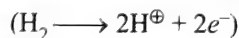
$$\text{Eq} = \frac{\text{Volume of gas given in L or mL at STP}}{\text{Volume of (one) equivalent of a gas in L or mL at STP}}$$

For example, the equivalent of 1.12 L of H_2 gas at STP is

$$\text{Eq} = \frac{1.12 \text{ L}}{11.2 \text{ L}} = 0.1 \text{ Eq}$$

(1 mol of H_2 gas at STP = 22.4 L)

(1 Eq of H_2 gas at STP = 11.2 L, since n -factor = 2)

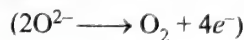


The equivalent of 1.12 L of O_2 gas at STP is

$$\text{Eq} = \frac{1.12 \text{ L}}{5.6 \text{ L}} = 0.2 \text{ Eq}$$

(1 mol of O_2 gas at STP = 22.4 L)

1 Eq of O_2 gas at STP = 5.6 L, since n -factor = 4)



Note: Calculation of n -factor or valency factor has been described in Chapter 2.

List of n -factor for some compounds

1. a. $\text{H}_2\text{C}_2\text{O}_4$ as an acid (2H^\oplus), ($n = 2$)
 b. $\text{H}_2\text{C}_2\text{O}_4$ as a reducing agent:
 $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^-$ ($n = 2$)
2. a. H_2O_2 as a reducing agent:
 $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2e^- + 2\text{H}^\oplus$ ($n = 2$)
 b. H_2O_2 as an oxidising agent:
 $2\text{H}^\oplus + 2e^- + \text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ ($n = 2$)
3. KMnO_4 as an oxidising agent:
 a. $\text{MnO}_4^\ominus + 5e^- + 8\text{H}^\oplus \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ ($n = 5$)
 (acidic medium)
 b. $e^- + \text{MnO}_4^\ominus \longrightarrow \text{MnO}_4^{2-}$ ($n = 1$)
 (strongly basic medium)
 c. $3e^- + \text{MnO}_4^\ominus + 4\text{H}^\oplus \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ ($n = 3$)
 (neutral medium or mild basic medium)
4. $\text{Na}_2\text{S}_2\text{O}_3$ as a reducing agent:
 a. $2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + 2e^-$ $\left(n = \frac{2}{2} = 1 \right)$
 (acidic medium)
 b. $\text{S}_2\text{O}_3^{2-} + 10\text{OH}^\ominus \longrightarrow 2\text{SO}_4^{2-} + 5\text{H}_2\text{O} + 8e^-$ ($n = 8$)
 (basic medium)
 c. $\text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} \longrightarrow 2\text{HSO}_4^\ominus + 8e^- + 8\text{H}^\oplus$ ($n = 8$)
 (neutral medium)
5. a. FeSO_4 as an reducing agent:
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ ($n = 1$)
 b. As an oxidising agent:
 $\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$ ($n = 2$)
6. $\text{Fe}_2(\text{SO}_4)_3$ as an oxidising agent:
 $2\text{Fe}^{3+} + 2e^- \longrightarrow 2\text{Fe}^{2+}$ ($n = 2$)
7. HNO_3 :
 a. As an acid:
 $\text{HNO}_3 \longrightarrow \text{H}^\oplus$ ($n = 1$)
 b. As an oxidising agent (conc HNO_3):
 $e^- + \text{NO}_3^\ominus + 2\text{H}^\oplus \longrightarrow \text{NO}_2 + \text{H}_2\text{O}$ ($n = 1$)

- c. Dil HNO_3 :
- $4\text{H}^{\oplus} + \text{NO}_3^{\ominus} + 3e^- \longrightarrow \text{NO} + 2\text{H}_2\text{O} \quad (n = 3)$
 - With Zn, Fe, Sn, Dil HNO_3 gives $\text{N}_2\text{O}(\text{g})$
 $2\text{NO}_3^{\ominus} + 10\text{H}^{\oplus} + 8e^- \longrightarrow \text{N}_2\text{O} + 5\text{H}_2\text{O}$
('n' factor = $8/2 = 4$)
- d. Cold dil HNO_3 :
 $7\text{H}^{\oplus} + 6e^- + \text{NO}_3^{\ominus} \longrightarrow \text{NH}_2\text{OH} + 2\text{H}_2\text{O} \quad (n = 6)$
- e. Very dil HNO_3 :
 $10\text{H}^{\oplus} + 8e^- + \text{NO}_3^{\ominus} \longrightarrow \text{NH}_4^{\oplus} + 3\text{H}_2\text{O} \quad (n = 8)$
8. NaHC_2O_4 :
- As an acid:
 $\text{HC}_2\text{O}_4^{\ominus} \longrightarrow \text{H}^{\oplus} \quad (n = 1)$
 - As an reducing agent:
 $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^- \quad (n = 2)$
9. NaHSO_3 :
- As an acid:
 $\text{HSO}_3 \longrightarrow \text{H}^{\oplus} \quad (n = 1)$
 - As a reducing agent:
 $\text{H}_2\text{O} + \text{HSO}_3^{\ominus} \longrightarrow \text{SO}_4^{2-} + 2e^- + 3\text{H}^{\oplus} \quad (n = 2)$
10. MnO_2 as a mild oxidising agent:
 $4\text{H}^{\oplus} + 2e^- + \text{MnO}_2 \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (n = 2)$
11. KClO_3 :
- As reducing agent:
 $\text{H}_2\text{O} + \text{ClO}_3^{\ominus} \longrightarrow \text{ClO}_4^{\ominus} + 2e^- + 2\text{H}^{\oplus} \quad (n = 2)$
 - As an oxidising agent
 $2\text{H}^{\oplus} + \text{ClO}_3^{\ominus} + 2e^- \longrightarrow \text{ClO}_2^{\ominus} + \text{H}_2\text{O} \quad (n = 2)$
12. As_2O_3 as reducing agent:
 $5\text{H}_2\text{O} + \text{As}_2\text{O}_3 \longrightarrow 2\text{AsO}_4^{3-} + 10\text{H}^{\oplus} + 4e^- \quad (n = 4)$
13. SO_2 as a reducing agent:
 $2\text{H}_2\text{O} + \text{SO}_2 \longrightarrow \text{SO}_4^{2-} + 2e^- + 4\text{H}^{\oplus} \quad (n = 2)$
14. HI as a reducing agent:
 $2\text{I}^{\ominus} \longrightarrow \text{I}_2 + 2e^- \quad \left(n = \frac{2}{2} = 1\right)$
15. I_2 as a reducing agent:
 $6\text{H}_2\text{O} + \text{I}_2 \longrightarrow 2\text{IO}_3^{\ominus} + 10e^- + 12\text{H}^{\oplus} \quad (n = 10)$
16. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ as an oxidising agent:
 $\text{Cr}_2\text{O}_7^{2-} + 6e^- + 14\text{H}^{\oplus} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (n = 6)$
17. FeC_2O_4 (ferrous oxalate) as a reducing agent:

$$\left[\begin{array}{l} \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^- \\ \text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^- \end{array} \right] \quad (n = 3)$$
18. $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ (ferric oxalate) as a reducing agent:

$$\left[\begin{array}{l} 3\text{C}_2\text{O}_4^{2-} \longrightarrow 6\text{CO}_2 + 6e^- \\ \text{Fe}^{3+} \text{ does not change} \end{array} \right] \quad (n = 6)$$
19. KBrO_3 as an oxidising agent
 $12\text{H}^{\oplus} + 10e^- + 2\text{BrO}_3^{\ominus} \longrightarrow \text{Br}_2 + 6\text{H}_2\text{O} \quad \left(n = \frac{10}{2} = 5\right)$
 $6\text{H}^{\oplus} + 6e^- + \text{BrO}_3^{\ominus} \longrightarrow \text{Br}^{\ominus} + 3\text{H}_2\text{O} \quad (n = 6)$
20. SeO_3^{2-} as a reducing agent:
 $\text{H}_2\text{O} + \text{SeO}_3^{2-} \longrightarrow \text{SeO}_4^{2-} + 2e^- + 4\text{H}^{\oplus} \quad (n = 2)$
21. AsO_2^{\ominus} as a reducing agent:
 $2\text{H}_2\text{O} + \text{AsO}_2^{\ominus} \longrightarrow \text{AsO}_4^{3-} + 2e^- + 4\text{H}^{\oplus} \quad (n = 2)$
22. Cu_2S (cuprous sulphide) as a reducing agent:

$$\left[\begin{array}{l} \text{Cu}_2\text{S} \longrightarrow 2\text{Cu}^{\oplus} + \text{S}^{2-} \\ \text{Cu}_2^{\oplus} \longrightarrow 2\text{Cu}^{2+} + 2e^- \\ 2\text{H}_2\text{O} + \text{S}^{2-} \longrightarrow \text{SO}_2 + 6e^- + 4\text{H}^{\oplus} \end{array} \right] \quad (n = 8)$$
23. CuS (cupric sulphide) as a reducing agent:

$$\left[\begin{array}{l} \text{CuS} \longrightarrow \text{Cu}^{2+} + \text{S}^{2-} \\ \text{S}^{2-} + 2\text{H}_2\text{O} \longrightarrow \text{SO}_2 + 6e^- + 4\text{H}^{\oplus} \end{array} \right] \quad (n = 6)$$
24. $\text{Sn} \longrightarrow \text{Sn}^{2+} + 2e^- \quad (n = 2)$
 $\text{Sn} \longrightarrow \text{Sn}^{4+} + 4e^- \quad (n = 4)$
25. $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^- \quad (n = 2)$
 $\text{Fe} \longrightarrow \text{Fe}^{3+} + 3e^- \quad (n = 3)$
26. $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^- \quad (n = 2)$
 $\text{Cu} \longrightarrow \text{Cu}^{1+} + e^- \quad (n = 1)$
27. $\text{Fe}(\text{NO}_2)_2$ (ferrous nitrite) as a reducing agent:

$$\left[\begin{array}{l} \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^- \\ 2\text{NO}_2^{\ominus} \longrightarrow 2\text{NO}_3^{\ominus} + 4e^- \end{array} \right] \quad (n = 5)$$
28. $\text{Fe}(\text{NO}_2)_3$ (ferric nitrite) as a reducing agent:

$$\left[\begin{array}{l} \text{Fe}^{3+} \text{ does not change} \\ 3\text{NO}_2^{\ominus} \longrightarrow 3\text{NO}_3^{\ominus} + 6e^- \end{array} \right] \quad (n = 6)$$
29. $\text{KClO}_3 \xrightarrow{\Delta} \text{KCl} + \text{O}_2 \quad (n = 6)$

Iodimetric and iodometric titrations:

S.No.	Estimation of	Reaction	Relation between oxidising agent and reducing agent
1.	I_2 (Iodimetry)	Titrating solution is $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Hypo) $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ or $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^{\ominus} + \text{S}_4\text{O}_6^{2-}$	$\text{I}_2 \equiv 2\text{I}^{\ominus} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $w(\text{Na}_2\text{S}_2\text{O}_3) = \frac{M}{1}$
2.	CuSO_4 (Iodometry)	$2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$ or $2\text{Cu}^{2+} + 4\text{I}^{\ominus} \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$ (white ppt)	$2\text{CuSO}_4 \equiv \text{I}_2 \equiv 2\text{I}^{\ominus} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $E_w \text{ of } \text{CuSO}_4 = \frac{M}{1}$

3.	Estimation of available Cl_2 in CaOCl_2 $\text{Cl}_2 + 2\text{I}^\ominus \longrightarrow 2\text{Cl}^\ominus + \text{I}_2$	$\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$	$\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I}^\ominus \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of CaOCl}_2 = \frac{M}{2}$
4.	MnO_2 present in pyrolusite	$\text{MnO}_2 + 4\text{HCl (conc)} \xrightarrow{\Delta} \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ or $\text{MnO}_2 + 4\text{H}^\oplus + 2\text{Cl}^\ominus \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2$ $\text{Cl}_2 + 2\text{I}^\ominus \longrightarrow \text{I}_2 + 2\text{Cl}^\ominus$	$\text{MnO}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I}^\ominus \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of MnO}_2 = \frac{M}{2}$
5.	IO_3^\ominus	$\text{IO}_3^\ominus + 5\text{I}^\ominus + 6\text{H}^\oplus \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{IO}_3^\ominus \equiv 3\text{I}_2 \equiv 6\text{I}^\ominus \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of MnO}_2 = \frac{M}{2}$
6.	H_2O_2	$\text{H}_2\text{O}_2 + 2\text{I}^\ominus + 2\text{H}^\oplus \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$	$\text{H}_2\text{O}_2 \equiv \text{I}_2 \equiv 2\text{I}^\ominus \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of H}_2\text{O}_2 = \frac{M}{2}$
7.	Cl_2	$\text{Cl}_2 + 2\text{I}^\ominus \longrightarrow 2\text{Cl}^\ominus + \text{I}_2$	$\text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I}^\ominus \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of Cl}_2 = \frac{M}{2}$
8.	O_3	$\text{O}_3 + 6\text{I}^\ominus + 6\text{H}^\oplus \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{O}_3 \equiv 3\text{I}_2 \equiv 6\text{I}^\ominus \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of O}_3 = \frac{M}{6}$
9.	ClO^\ominus	$\text{ClO}^\ominus + 2\text{I}^\ominus + 2\text{H}^\oplus \longrightarrow \text{H}_2\text{O} + \text{Cl}^\ominus + \text{I}_2$	$\text{ClO}^\ominus \equiv \text{I}_2 \equiv 2\text{I}^\ominus \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Ew of ClO}^\ominus = \frac{M}{2}$
10.	$\text{Cr}_2\text{O}_7^{2-}$	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^\oplus + 6\text{I}^\ominus \longrightarrow 3\text{I}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$\text{Cr}_2\text{O}_7^{2-} \equiv 3\text{I}_2 \equiv 6\text{I}^\ominus$ $\text{Ew of Cr}_2\text{O}_7^{2-} = \frac{M}{6}$

3.1 INTRODUCTION

In this chapter, basic concepts of solving stoichiometric problems are explained. Generally, two methods are employed for solving stoichiometric problems based on redox reactions:

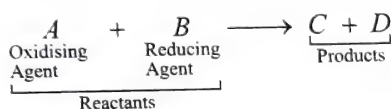
- Balancing redox reactions followed by solving the problem as a simple balanced equation using the mole concept.
- Using the concept of gram equivalent or milli equivalent as used in neutralisation.

mEq or g mEq of reducing agent = mEq or g mEq of oxidising agent.

These involve mole concept, gram equivalent, and their applications in various chemical processes.

3.2 GRAM EQUIVALENT

According to the concept of gram equivalent or mEq, there is no need to balance a redox reaction. For example,



1 g Eq of A \equiv 1 g Eq of B \equiv 1 g Eq of C \equiv 1 g Eq of D
or

mEq of an oxidising agent = mEq of a reducing agent

3.3 EQUIVALENT WEIGHT (EW) OF SOME OXIDANTS AND REDUCTANTS

1. Potassium permanganate (KMnO₄)

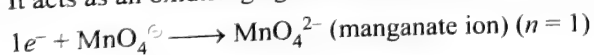
(Atomic weight of K is 39, Mn is 55, and O is 16)

- It acts as an oxidising agent in acidic medium.



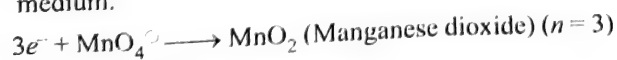
$$Ew(\text{KMnO}_4/\text{H}^+) = \frac{39 + 55 + 16 \times 4}{5} = \frac{158}{5} = 31.6 \text{ g}$$

- It acts as an oxidising agent in strong basic medium:



$$Ew(\text{KMnO}_4/\text{OH}^-) = \frac{158}{1} = 158 \text{ g}$$

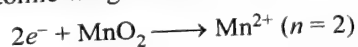
- It acts as an oxidising agent in dilute basic or neutral medium.



$$Ew(\text{KMnO}_4) = \frac{158}{3} = 52.66 \text{ g}$$

2. Manganese dioxide (MnO₂) acts as oxidising agent in acidic medium.

(Atomic weight of Mn is 55)



$$Ew(\text{MnO}_2) = \frac{55 + 16 \times 2}{2} = \frac{87}{2} = 43.5 \text{ g}$$

3. Potassium dichromate (K₂Cr₂O₇) acts as an oxidising agent only.

(Atomic weight of K is 39 and Cr is 52)



$$Ew(\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+) = \frac{39 \times 2 + 52 \times 2 + 16 \times 7}{6} = \frac{294}{6} = 49.0 \text{ g}$$

$$Ew(\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+) = \frac{23 \times 2 + 52 \times 2 + 16 \times 7}{6} = \frac{262}{6} = 43.66 \text{ g}$$

4. Ferrous sulphate (FeSO₄) acts both as an oxidising agent and a reducing agent.

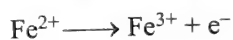
(Atomic weight of Fe is 56, S is 32)

As an oxidising agent



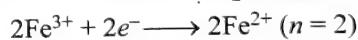
$$Ew(\text{FeSO}_4) = \frac{56 + 32 + 16 \times 4}{2} = \frac{152}{2} = 76.0 \text{ g}$$

As an reducing agent



$$Ew(\text{FeSO}_4) = \frac{152}{1} = 152.0 \text{ g}$$

5. Ferric sulphate [Fe₂(SO₄)₃] acts as an oxidising agent only.



$$Ew[\text{Fe}_2(\text{SO}_4)_3] = \frac{56 \times 2 + 3(32 + 16 \times 4)}{2} = \frac{112 + 288}{2} = \frac{400}{2} = 200.0 \text{ g}$$

6. a. Oxalic acid (H₂C₂O₄·2H₂O) acts as a reducing agent

$$Mw \text{ of } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 2 + 2 \times 12 + 16 \times 4 + 2 \times 18 = 126.0 \text{ g}$$

$$Mw \text{ of } \text{H}_2\text{C}_2\text{O}_4 = 92.0 \text{ g}$$

$$Mw \text{ of } \text{Na}_2\text{C}_2\text{O}_4$$

$$= \frac{2 \times 23 + 2 \times 12 + 16 \times 4}{2}$$

$$= \frac{134}{2} = 67.0 \text{ g}$$

$$Mw \text{ of } \text{C}_2\text{O}_4^{2-} = 90.0 \text{ g}$$

$$Mw \text{ of } \text{CaC}_2\text{O}_4$$

$$= \frac{40 + 88}{2} = \frac{128}{2} = 64.0 \text{ g}$$

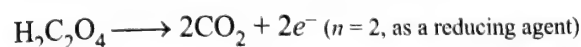
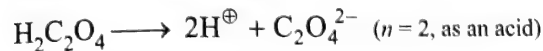


$$Ew \text{ of } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \frac{126}{2} = 63.0 \text{ g}$$

$$Ew(H_2C_2O_4) = \frac{92}{2} = 46.0 \text{ g}$$

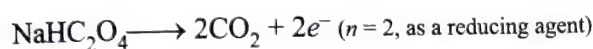
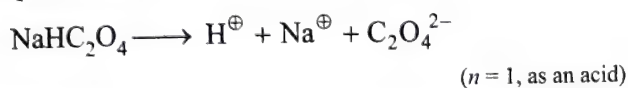
$$Ew \text{ of } C_2O_4^{2-} = \frac{90}{2} = 45.0 \text{ g}$$

- b. **Oxalic acid** acts as acids and reducing agent or oxidising agent in different experiments. For example,

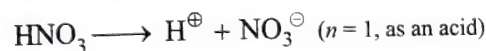


- c. **(NaHC₂O₄ or KHC₂O₄)**

Sodium or potassium hydrogen oxalate acts as acids and reducing agent or oxidising agent in different experiments.



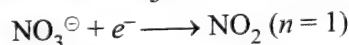
7. a. **Nitric acid (HNO₃)** acts as acids and reducing agent or oxidising agent in different experiments.



$$Ew \text{ of } HNO_3 = \frac{1 + 14 + 16 \times 3}{1} = 63.0 \text{ g}$$

- b. **Nitric acid** acts as oxidising agent. The equivalent weight of HNO₃ depends on dilution.

- a. **Conc HNO₃:**



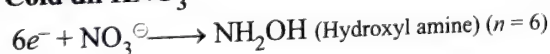
$$Ew = 63.0 \text{ g}$$

- b. **Dil HNO₃:**



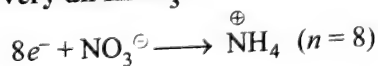
$$Ew = \frac{63}{3} = 21.0 \text{ g}$$

- c. **Cold dil HNO₃:**



$$Ew = \frac{63}{6} = 10.5 \text{ g}$$

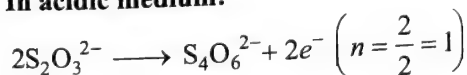
- d. **Very dil HNO₃:**



$$Ew = \frac{63}{8} = 7.875 \text{ g}$$

8. **Sodium thiosulphate (Na₂S₂O₃)** acts as a reducing agent.
(Molecular weight of Na₂S₂O₃ = 2 × 23 + 2 × 32 + 3 × 16 = 158)

- a. **In acidic medium:**



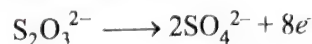
(Tetrathionate ion)

$$\text{For 2 mol of Na}_2\text{S}_2\text{O}_3, n = 2, \text{ and for 1 mol} = \frac{2}{2} = 1$$

$$Ew \text{ of } (Na_2S_2O_3) = \frac{158}{1} = 158.0 \text{ g}$$

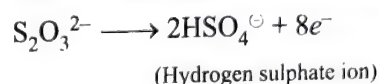
$$\begin{aligned} \text{b. } Ew \text{ of } (Na_2S_2O_3 \cdot 5H_2O) &= \frac{Mw}{1} = \frac{158 + 5 \times 18}{1} \\ &= \frac{158 + 90}{1} = 248.0 \text{ g} \end{aligned}$$

- c. **In basic medium:**



$$Ew (Na_2S_2O_3 / OH^{\ominus}) = \frac{158}{8} = 19.75 \text{ g}$$

- d. **In neutral or aqueous medium:**

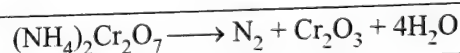
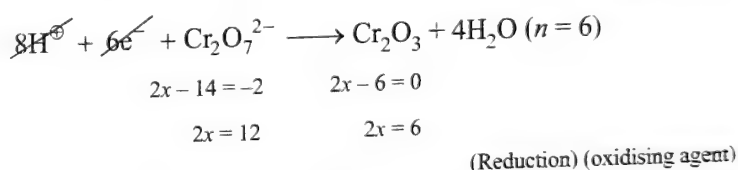
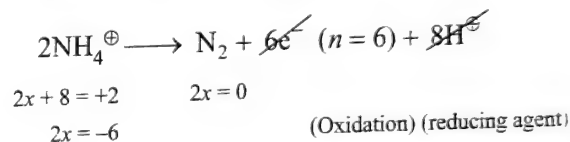


(Hydrogen sulphate ion)

$$Ew (Na_2S_2O_3) = \frac{158}{8} = 19.75 \text{ g}$$

9. **Ammonium dichromate [(NH₄)₂Cr₂O₇]:**

NH_4^{\oplus} (ammonium ion) is oxidised to N₂ and Cr₂O₇²⁻ (dichromate ion) is reduced to Cr₂O₃.



3.4 STOICHIOMETRIC CALCULATIONS

In this section, we will discuss problems based on balanced chemical equations and application of mole concept.

The analysis of a chemical reaction is generally carried out in the form of mass of reacting species taking part in a given reaction (*gravimetric analysis*) or in terms of concentrations of reacting species taking part in a given reaction (*volumetric analysis*).

In gravimetric analysis, we generally analyse reactions such as decomposition of compounds under heat to produce a residue and gas, displacement reactions, and action of acids on metals, or simple balanced chemical equations involving weight (solid)–volume (gas) relationships.

In volumetric analysis, we generally analyse neutralisation and redox titrations involving aqueous solutions in general.

Neutralisation

A reaction in which an acid (or base) completely reacts with a base (or an acid) to form salt and water is called *neutralisation*. If HA is an acid, BOH is a base, and BA is a salt, then neutralisation reaction can be represented as follows:

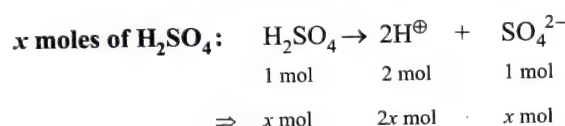
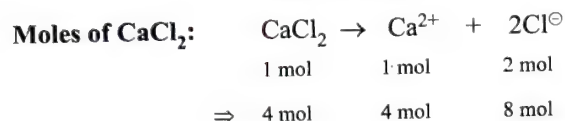
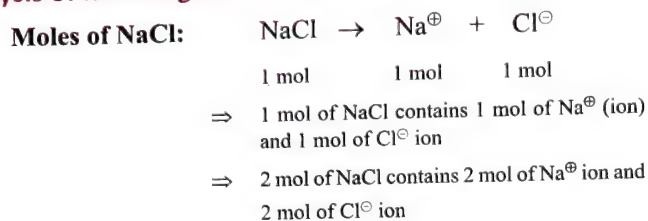


Redox Reactions

A reaction in which both oxidation and reduction take place simultaneously is called as *redox reaction*. A redox reaction always involves a pair of an *oxidising* and a *reducing agent*.

Note: Redox reactions have been discussed in Chapter 2.

Analysis of Meaning of Some Terms



3.4.1 Application of Mole Concept in a Balanced Chemical Equation

Consider a general balanced chemical reaction or equation



where A and B are reactants, C and D are products, and m , n , p , and q are stoichiometric coefficients.

The above balanced reaction is analysed as follows:
 m moles of A react with n moles of B to produce p moles of C plus q moles of D.

This can be represented (written) as:

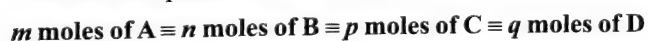
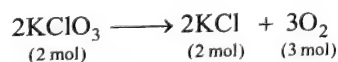


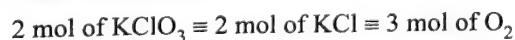
Illustration of the Mole Concept

What weight of KCl (potassium chloride) formed on heating 12.25 g of KClO_3 ? Also calculate the weight of O_2 liberated.

First write a balanced chemical equation for the decomposition of KClO_3 .

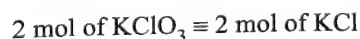


From stoichiometry, we have



$$\text{moles of } \text{KClO}_3 = \frac{12.25}{122.5} = 0.1 \quad \left[\begin{array}{l} Mw(\text{KClO}_3) = 122.5 \\ \text{moles} = \frac{\text{Wt.}}{Mw} \\ Mw(\text{KCl}) = 74.5 \end{array} \right]$$

Now,



$$\equiv 0.1 \times 74.5 \text{ g of KCl}$$

$$[\text{g} = \text{moles} \times M_0]$$

$$\equiv 7.45 \text{ g of KCl is formed}$$



$$\Rightarrow 0.1 \text{ mol of } \text{KClO}_3 \equiv \frac{3}{2} \times 0.1 \text{ mol of } \text{O}_2$$

$$\equiv \frac{3}{2} \times 0.1 \times 32 \text{ g of } \text{O}_2$$

$$\equiv 4.8 \text{ g of } \text{O}_2$$

Problem-Solving Technique Using Mole Concept

Follow the given sequence:

1. First write a balanced chemical equation.
2. Analyse the reactants and products according to their respective stoichiometric coefficients, i.e. m mol of A $\equiv n$ mol of B $\equiv p$ mol of C $\equiv q$ mol of D.
3. According to the data given, proceed as explained in the above illustration.
4. In stoichiometric problems involving gases, we assume all gases to be ideal and apply gas equation $PV = nRT$.

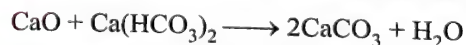
(P is the pressure of gas in atm, V is the volume of gas in L, and T is the temperature in kelvin, and R is the universal gas constants having value $0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$)

- a. At STP, the volume occupied by 1 mol of a gaseous compound is equal to 22.4 L (or 22400 mL). This is also called **molar volume**. If the pressure is 1 bar, the volume of gas is 22.7 L.
- b. At room temperature, $T = 298 \text{ K}$, $P = 1.0 \text{ atm}$, volume of 1 mol of gas is 24.48 L. It is also called SATP (standard ambient temperature and pressure) conditions. If the pressure is 1 bar, the volume of a gas is 24.7 L.
- c. $1 \text{ atm} = 760 \text{ mm Hg column}$
- d. $1 \text{ atm} = 1.01325 \text{ bar} = 101.325 \text{ kPa} = 101325 \text{ Pa} = 101325 \text{ N m}^{-2}$
- e. $1 \text{ bar} = 0.986 \text{ atm}$

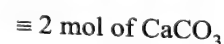
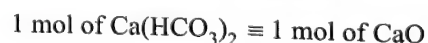
For example:

Calculate the weight of CaO required to remove the hard-ness of 10^6 L of water containing 1.62 g of $\text{Ca}(\text{HCO}_3)_2$ in 1.0 L .

Sol. Consider the reaction between CaO and $\text{Ca}(\text{HCO}_3)_2$.



From stoichiometry, we have



Now moles of bicarbonate in 1.0 L of sample is

$$\frac{1.62}{162} = 0.01 [Mw \text{ of } \text{Ca}(\text{HCO}_3)_2 = 162]$$

moles of CaO required for 10^6 L of water

$$= 0.01 \times 10^6 = 10^4 \text{ mol}$$

moles of CaO required for 1.0 L of sample
= 0.01 (from stoichiometry)

grams of CaO = $10^4 \times 56 = 5.6 \times 10^5$ g

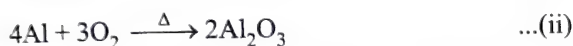
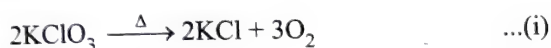
5. **Yield of a chemical reaction:** In any chemical reaction, the amount of product formed is always less than the calculated amount due to reversibilities in the chemical reaction. Therefore, the yield of a chemical reaction (Y) comes into picture and is given by

$$Y = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

6. **Sequential reaction:** In general, to get the desired product, the process follows a series of reactions in which the product of one reaction is taken as the starting material of the next reaction. These reactions are known as *sequential reactions*.

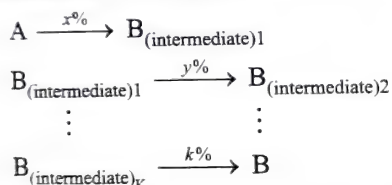
For example:

In the formation of Al_2O_3 from KClO_3 , the following sequential reactions take place

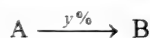


Oxygen produced in reaction (i) is taken as the starting material for reaction (ii).

Yield in a sequential reaction: If a sequential reaction in the formation of a compound B from a compound A follows



where $x\%$ and $y\%$ are yields of the respective reactions in the process chain, then the yield of the reaction



is given by the product of the yields of all the intermediate reactions, i.e.

$$Y\% = \left(\frac{x}{100} \times \frac{y}{100} \times \dots \times \frac{k}{100} \right) \times 100\%$$

ILLUSTRATION 3.1

H_2SO_4 acts as

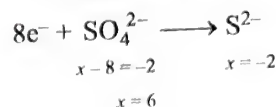
- An acid
- An oxidising agent
- A dehydrating agent

Select equations from the following which explain each type of behaviour.

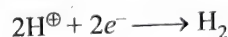
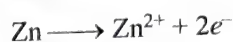
- $5\text{H}_2\text{SO}_4(\text{conc}) + 4\text{Zn} \longrightarrow 4\text{Zn}^{2+} + \text{H}_2\text{S} + 4\text{SO}_4^{2-} + 4\text{H}_2\text{O}$
- $\text{H}_2\text{SO}_4(\text{dil}) + \text{Zn} \longrightarrow \text{Zn}^{2+} + \text{H}_2 + \text{SO}_4^{2-}$
- $\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{H}_2\text{SO}_4(\text{conc})} 6\text{C} + 6\text{H}_2\text{O}$
- $\text{H}_2\text{SO}_4(\text{dil}) + \text{ZnCO}_3 \longrightarrow \text{Zn}^{2+} + \text{CO}_2 + \text{SO}_4^{2-} + \text{H}_2\text{O}$

Sol.

- H_2SO_4 acts as oxidising agent, in which SO_4^{2-} is reduced to S^{2-} (sulphide ion)



- H_2SO_4 acts as an acid and an oxidising agent. All strong acids can liberate H_2 with an active metal such as Zn, unless another part of the molecule is more easily reduced.



- H_2SO_4 acts as a dehydrating agent since it removes H_2O from $\text{C}_6\text{H}_{12}\text{O}_6$.

- H_2SO_4 acts as an acid since Zn^{2+} in ZnCO_3 and SO_4^{2-} in H_2SO_4 does not change, only H^+ ions in H_2SO_4 reacts with CO_3^{2-} to give CO_2 and H_2O .



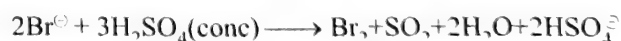
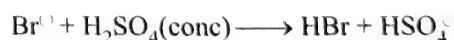
ILLUSTRATION 3.2

- NaBr on reaction with conc H_2SO_4 gives SO_2 , HBr, and Br_2 , whereas NaCl with conc H_2SO_4 gives HCl but no Cl_2 or SO_2 is produced. Explain.
- Which of the following reactions occur?
 - $\text{Br}_2 + 2\text{NaCl} \longrightarrow \text{Cl}_2 + \text{NaBr}$
 - $\text{Cl}_2 + \text{NaBr} \longrightarrow \text{Br}_2 + 2\text{NaCl}$

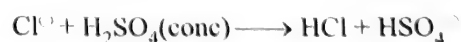
Sol.

- Since the reduction potential of $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$, F_2 can oxidise Cl^- , Br^- , and I^- but not vice versa. Similarly, Cl_2 can oxidise Br^- and I^- but not vice versa. Likewise, Br_2 can oxidise I^- only but not vice versa.

Br^- is more easily oxidised than Cl^- . So NaBr (Br^-) on reaction with conc H_2SO_4 , undergoes oxidation to Br_2 whereas H_2SO_4 (SO_4^{2-}) is reduced to SO_2 . So the reaction of NaBr with conc H_2SO_4 is as follows:



Reaction of NaCl with conc H_2SO_4 ,



- From the above equations it is clear that Br^- is more easily oxidised than Cl^- .

Hence, Cl_2 will oxidise Br^- but not vice versa. So reaction (ii) is feasible.

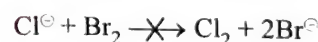
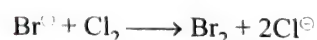


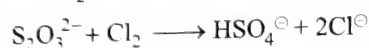
ILLUSTRATION 3.3

Which of the following is correct?

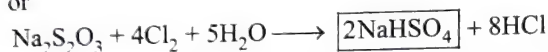
- i. Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives
 a. $\text{Na}_2\text{S}_4\text{O}_6$ b. NaHSO_4 c. NaCl d. NaOH
- ii. Acidic solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives
 a. $\text{Na}_2\text{S}_4\text{O}_6$ b. NaHSO_4 c. Na_2SO_4 d. NaOH
- iii. Basic solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives
 a. NaOH b. $\text{Na}_2\text{S}_4\text{O}_6$ c. Na_2SO_4 d. NaHSO_4

Sol.

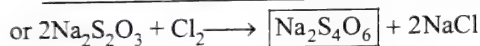
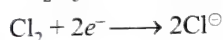
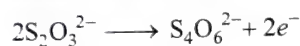
- i. a. $\text{S}_2\text{O}_3^{2-}$ in aqueous or neutral medium is oxidised to HSO_4^\ominus , and Cl_2 is reduced to Cl^\ominus .



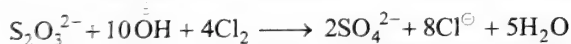
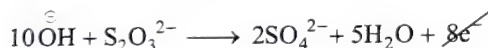
or



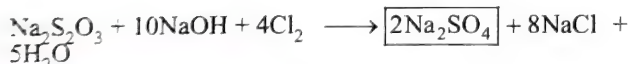
- ii. a. $\text{S}_2\text{O}_3^{2-}$ in acidic medium is oxidised to $\text{S}_4\text{O}_6^{2-}$ (tetrathionate ion), and Cl_2 is reduced to Cl^\ominus .



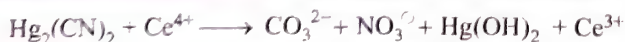
- iii. c. $\text{S}_2\text{O}_3^{2-}$ in basic medium is oxidised to SO_4^{2-} , and Cl_2 is reduced to Cl^\ominus .



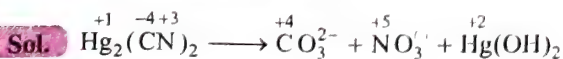
or

**ILLUSTRATION 3.4**

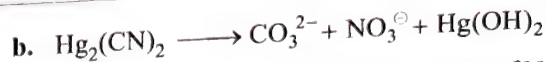
Complete and balance the following equations in basic solution:



- a. By considering the carbon in $\text{Hg}_2(\text{CN})_2$, in -4 oxidation state and the nitrogen in $+3$ oxidation state.
- b. By considering C in $+4$ oxidation state and N in $+5$ oxidation state.
- c. By considering Hg in $+2$ and C in -4 oxidation state.
- d. Explain why the same result is obtained regardless of the choice of oxidation state.



- a. If the oxidation state of C is -4 and that of N is $+3$, then the oxidation state of Hg is $+1$. In the products, oxidation numbers are $+4$, $+5$, and $+2$, respectively. The total increase in oxidation number is 22.



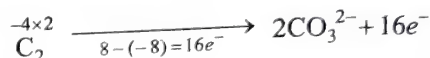
If the oxidation state of C is $+4$ and that of N is $+5$, then that of Hg must be -9 .

Then the only element oxidised is Hg, and the total increase in oxidation number is again 22.

The oxidation number of Hg, -9 , is impossible, but it still gives the same change in oxidation number.

- c. If the oxidation state of Hg is $+2$ and C is -4 , then that of N must be $+2$. The oxidation still involves $+22$ change in oxidation number.

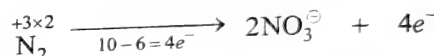
- d. No matter which set of oxidation number is used, as long as they total zero, the charge on the $\text{Hg}_2(\text{CN})_2$, the same number of electrons must be added to the half reaction.



$$2x = -8$$

$$2x - 12 = -4$$

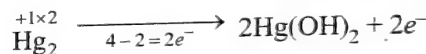
$$2x = 8$$



$$2x = 6$$

$$2x - 12 = -2$$

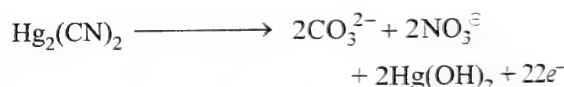
$$2x = 10$$



$$2x = 2$$

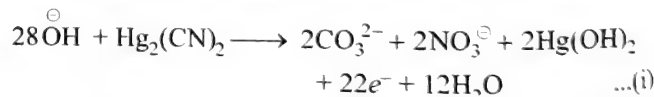
$$2x - 4 = 0$$

$$2x = 4$$

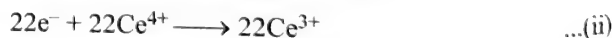


Now balance in basic medium:

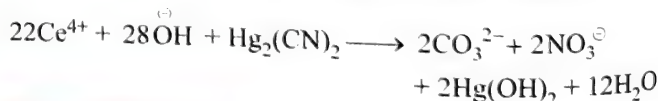
First balance charge by adding 28OH^\ominus to LHS and then balance the oxygen atom by adding $12\text{H}_2\text{O}$ to RHS.



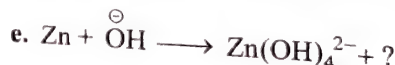
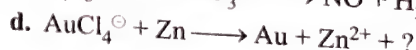
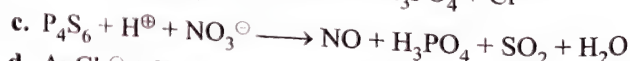
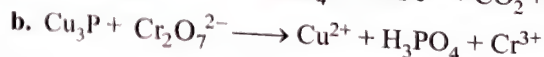
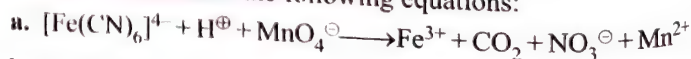
Now balance the reduction reaction



Add Eqs. (i) and (ii) to get the final redox reaction

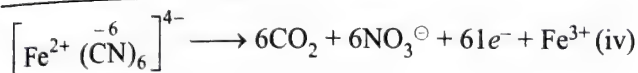
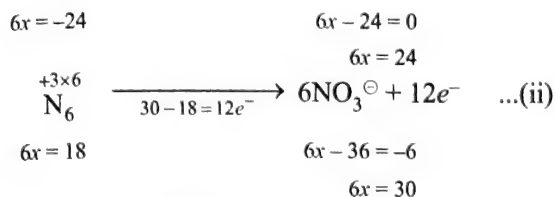
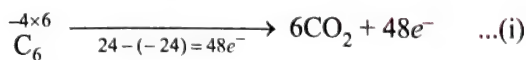
**ILLUSTRATION 3.5**

Complete and balance the following equations:

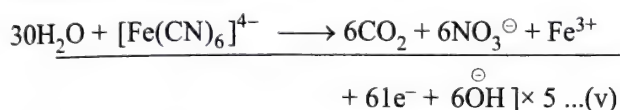




Proceed as in the above illustration.



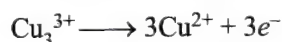
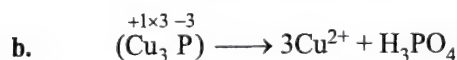
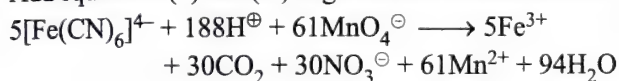
Balance Eq. (iv) in acidic medium.



Balance the reduction reaction of MnO_4^- to Mn^{2+}



Add equations (v) and (vi) to get the final redox reaction.

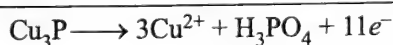


$$3x = 3 \quad 3x = 6$$

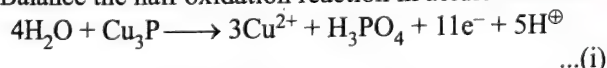


$$x = -3 \quad 3 + x - 8 = 0$$

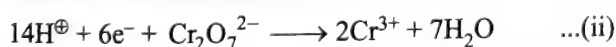
$$x = 5$$



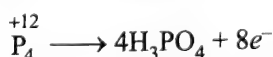
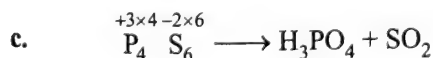
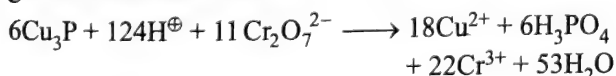
Balance the half oxidation reaction in acidic medium.



Balance the half reduction reaction of $\text{Cr}_2\text{O}_7^{2-}$ to 2Cr^{3+}



Multiply Eq. (i) by 6 and Eq. (ii) by 11 and add them to get the final redox reaction.



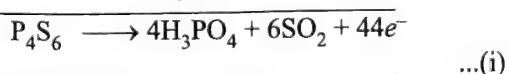
$$4x = 12 \quad 12 + 4x - 32 = 0$$

$$4x = 20$$

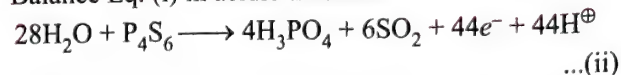


$$6x = -12 \quad 6x - 24 = 0$$

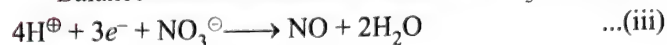
$$6x = 24$$



Balance Eq. (i) in acidic medium.



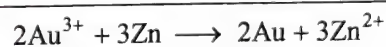
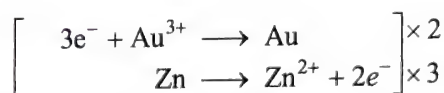
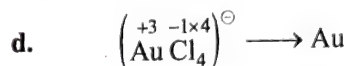
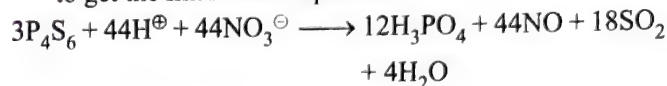
Balance the half reduction reaction of NO_3^- to NO .



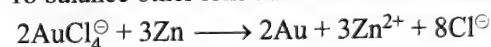
$$x - 6 = -1 \quad x - 2 = 0$$

$$x = 5 \quad x = 2$$

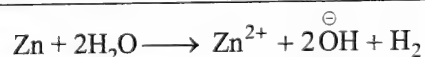
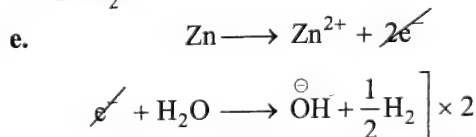
Multiply Eq. (ii) by 3 and Eq. (iii) by 44 and add them to get the final redox equation.



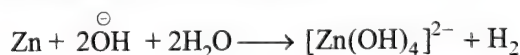
To balance other ions add 8Cl^- to both sides



Zn is oxidised to Zn^{2+} , so H_2O is reduced to OH^- and $1/2\text{H}_2$.



To balance other ions, add 2OH^- to both sides. So the net balanced redox equation is



CONCEPT APPLICATION EXERCISE 3.1

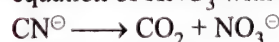
Subjective Type

1. Balance the following equation in basic medium



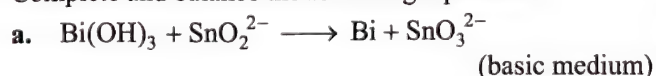
In the commercial preparation of HNO_3 by Ostwald process, the above reaction is carried out directly in the gaseous state. Explain why the same equation describes the direct reaction and the reaction in basic medium?

2. CN^- is oxidised by a strong oxidising agent to NO_3^- and CO_2 or CO_3^{2-} depending upon the acidity of the reaction mixture. HNO_3 , a strong oxidising agent is reduced by a moderate reducing agent to NO . Write the balanced equation of HNO_3 with KCN .

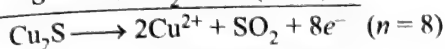
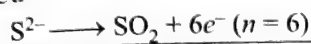
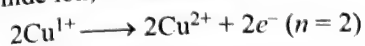


If this reaction is carried out, what safety precautions are required?

3. Complete and balance the following equations:

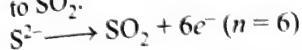


3. In cuprous sulphide (Cu_2S), both Cu^{\oplus} (cuprous ion) and S^{2-} (sulphide ion) are oxidised.



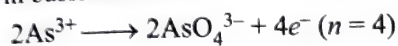
$$Ew(\text{Cu}_2\text{S}) = \frac{2 \times 63.5 + 32}{8} = \frac{159}{8} = 19.875 \text{ g}$$

4. In cupric sulphide (CuS) only S^{2-} ions not Cu^{2+} is oxidised to SO_2 .



$$Ew(\text{CuS}) = \frac{63.5 + 32}{6} = \frac{95.5}{6} = 15.91 \text{ g}$$

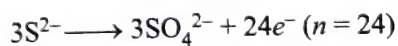
5. In Arsenic sulphide (As_2S_3) both As^{3+} and S^{2-} ions are oxidised in basic medium.



(Arsenate ion)

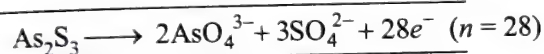
$$2x = 6 \quad 2x - 16 = -6$$

$$2x = 10$$



$$3x = -6 \quad 3x - 24 = -6$$

$$3x = 18$$



Atomic weight of As = 74.92, S = 32

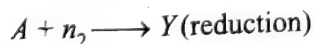
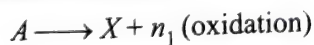
$$[Mw(\text{As}_2\text{S}_3)] = 2 \times 74.92 + 3 \times 32 = 245.84$$

$$Ew(\text{As}_2\text{S}_3) = \frac{245.84}{28} = 8.78 \text{ g}$$

3.4.4 Ew of a Compound in a Disproportionation Reaction

When the number of electron transfers is different in oxidation and reduction half reactions:

First method: Let compound A or ion A undergo disproportionation reaction to give X and Y ions, respectively, in oxidation and reduction reactions involving n_1 and n_2 number of electrons in oxidation and reduction reactions.



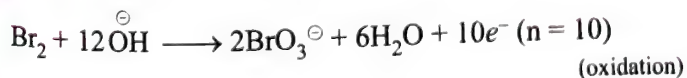
The equivalent weight of such reaction is shown below:

$$Ew = \left(\frac{\text{Molecular weight of } A}{n_1} + \frac{\text{Molecular weight of } A}{n_2} \right)$$

ILLUSTRATION 3.6

Br_2 undergoes disproportionation reaction in basic medium to give Br^{\ominus} ion and BrO_3^{\ominus} (bromate) ion in reduction and oxidation reactions.

Sol. $\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^{\ominus} \quad (n = 2) \text{ (reduction)}$



First method:

$$Ew(\text{Br}_2) = \frac{Mw(\text{Br}_2)}{2} + \frac{Mw(\text{Br}_2)}{10}$$

$$= \frac{80 \times 2}{2} + \frac{80 \times 2}{10} = 80 + 16 = 96 \text{ g}$$

Alternatively, $Ew(\text{Br}_2)$

$$= Mw(\text{Br}_2) \left(\frac{1}{2} + \frac{1}{10} \right)$$

$$= Mw(\text{Br}_2) \times \frac{6}{10}$$

$$= \frac{80 \times 2 \times 6}{10} = 96 \text{ g}$$

$$\therefore n\text{-factor of } \text{Br}_2 = \frac{10}{6}$$

$$\therefore Ew(\text{Br}_2) = \frac{Mw(\text{Br}_2)}{\text{mean } n\text{-factor}} = \frac{Mw(\text{Br}_2)}{10/6}$$

$$= \frac{6 \times Mw(\text{Br}_2)}{10}$$

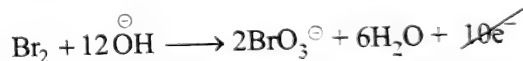
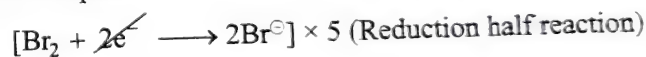
Second method:

$$Ew = \frac{\text{Effective molecular weight of a substance } A}{\text{Number of electron transfer}}$$

where effective molecular weight of A

$$= \left(\begin{array}{c} \text{Total molecular weight} \\ \text{of } A \text{ in oxidation} \\ \text{half reaction} \end{array} \right) + \left(\begin{array}{c} \text{Total molecular weight} \\ \text{of } A \text{ in reduction} \\ \text{half reaction} \end{array} \right)$$

For example:



Total change in number of electrons = 10

$$\text{Effective molecular weight of } \text{Br}_2 = 5 Mw(\text{Br}_2) + Mw(\text{Br}_2) = 6Mw(\text{Br}_2)$$

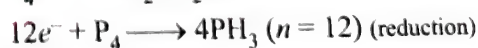
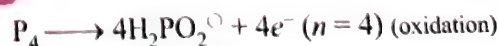
$$Ew(\text{Br}_2) = \frac{6Mw(\text{Br}_2)}{10} = \frac{6 \times 80 \times 2}{10} = 96 \text{ g}$$

$$\therefore n\text{-factor of } \text{Br}_2 = \frac{10}{6}$$

ILLUSTRATION 3.7

P_4 undergoes disproportionation in basic medium to give PH_3 (phosphine) and $\text{H}_2\text{PO}_2^{\ominus}$ (dihydrogen hypophosphite ion). Atomic weight of P is 31.

Sol.



First method:

$$Ew(\text{P}_4) = \frac{Mw(\text{P}_4)}{4} + \frac{Mw(\text{P}_4)}{12}$$

$$= \frac{31 \times 4}{4} + \frac{31 \times 4}{12}$$

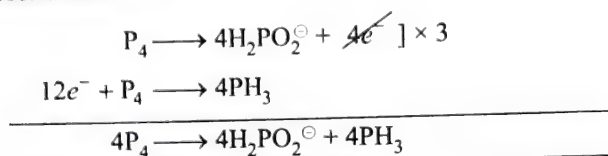
$$= 31 + \frac{31}{3} = 31 + 10.33 = 41.33 \text{ g}$$

Alternatively,

$$Ew(P_4) = Mw(P_4) \left(\frac{1}{4} + \frac{1}{12} \right) = Mw(P_4) \times \frac{1}{3}$$

$\therefore n$ -factor of $P_4 = 3$

Second method:



Total change in number of electrons = 12

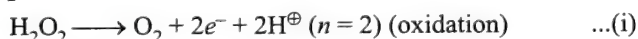
$$\begin{aligned} \text{Effective molecular weight of } P_4 &= Mw(P_4) + 3Mw(P_4) \\ &= 4Mw(P_4) \end{aligned}$$

$$Ew(P_4) = \frac{4Mw(P_4)}{12} = \frac{4 \times 4 \times 31}{12} = 41.33 \text{ g}$$

$$\therefore n\text{-factor of } P_4 = \frac{12}{4} = 3$$

3.4.5 Ew of a Compound in which Electron Transfers are Same in Oxidation and Reduction Half Reactions

H_2O_2 undergoes disproportionation in acid medium to give O_2 and H_2O .



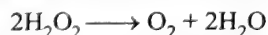
First method:

$$\begin{aligned} Ew(H_2O_2) &= \frac{Mw(H_2O_2)}{2} + \frac{Mw(H_2O_2)}{2} \\ &= Mw(H_2O_2) \left(\frac{1}{2} + \frac{1}{2} \right) \\ &= Mw(H_2O_2) = 34 \text{ g} \end{aligned}$$

Hence, n -factor of H_2O_2 in disproportionation reaction is 1.

Second method:

Adding Eqs. (i) and (ii), we get the net equation as follows:

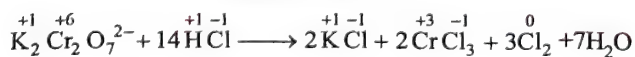
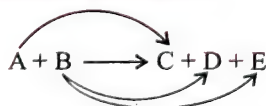


Total change in number of electrons = 2

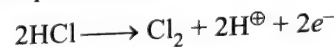
$$Ew(H_2O_2) = \frac{2 \times 34}{2} = 34 \text{ g}$$

Thus, n -factor of H_2O_2 in such case is 1.

3.4.6 Ew of a Reactant when a Part of it is Used as an Oxidising Agent or Reducing Agent and the Remaining Part is Consumed in the Formation of Products



In the above equation, Cl^\ominus from HCl goes in $CrCl_3$, Cl_2 and KCl . So the concept of mEq has to be used carefully.



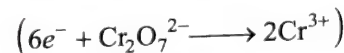
$$Ew(HCl) = \frac{Mw(HCl)}{1} \text{ is wrong}$$

In such cases, proceed as follows:

First method:

Use direct formula for such problems.

(n -factor of $Cr_2O_7^{2-} = 6$)



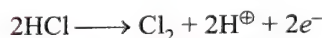
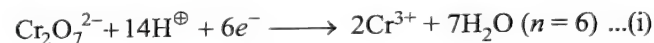
$\therefore n$ -factor for HCl

$$\begin{aligned} &= \frac{n\text{-factor of } Cr_2O_7^{2-} \text{ (oxidising agent)}}{\text{Number of moles of } HCl \text{ in balanced mole equation}} \\ &= \frac{6}{14} = \frac{3}{7} \end{aligned}$$

Therefore, Equivalent weight of 1 mol of HCl

$$= \frac{Mw(HCl)}{\frac{3}{7}} = \frac{36.5 \times 7}{3} = 85.16$$

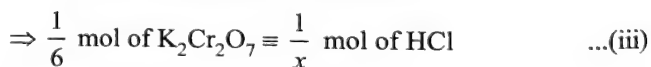
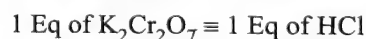
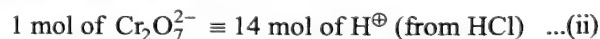
Second method: Balance the ionic equation



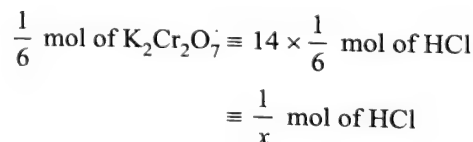
Note: n -factor for $HCl \neq 1$

Let the n -factor of HCl be x

According to Eq. (i),

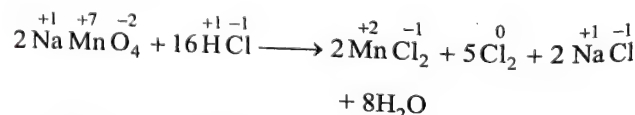


From Eq. (ii),



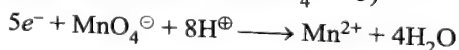
$$\Rightarrow \frac{14}{6} = \frac{1}{x} \Rightarrow x = \frac{6}{14} = \frac{3}{7}$$

$$n\text{-factor of } HCl \equiv \frac{3}{7}$$



Here, Cl^\ominus from HCl goes to $MnCl_2$, Cl_2 , and $NaCl$.

First method: (n -factor of $MnO_4^\ominus = 5$)



$$n\text{-factor of HCl} = \frac{n\text{-factor of } 2\text{MnO}_4^- \text{ (oxidising agent)}}{\text{Number of moles of HCl in balanced mole equation}}$$

$$= \frac{2 \times 5}{16} = \frac{5}{8}$$

Second method: Let the n -factor of HCl be x .

$$2 \text{ mol of NaMnO}_4 \equiv 16 \text{ mol of HCl}$$

$$1 \text{ mol of NaMnO}_4 \equiv 8 \text{ mol of HCl} \quad \dots(i)$$

$$1 \text{ Eq of NaMnO}_4 \equiv 1 \text{ Eq of HCl}$$

$$\frac{1}{5} \text{ mol of NaMnO}_4 \equiv \frac{1}{x} \text{ mol of HCl}$$

From Eq. (i), we get

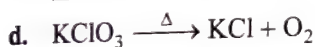
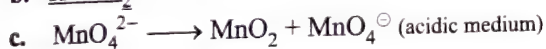
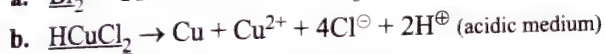
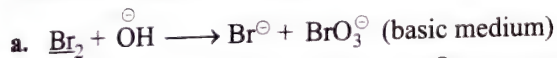
$$\frac{1}{5} \text{ mol of NaMnO}_4 \equiv 8 \times \frac{1}{5} \text{ mol of HCl} \equiv \frac{1}{x} \text{ mol of HCl}$$

$$\Rightarrow \frac{8}{5} = \frac{1}{x} \Rightarrow x = \frac{5}{8}$$

CONCEPT APPLICATION EXERCISE 3.2

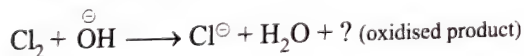
Subjective Type

1. Calculate the equivalent weight of the underlined species in the following unbalanced reactions:



2. a. What is the equivalent weight of (i) $\text{Fe}(\text{HC}_2\text{O}_4)_2$, (ii) $\text{Fe}(\text{HC}_2\text{O}_4)_3$ as reducing agent and acid.

- b. Equivalent weight of Cl_2 is 42.6 in the following disproportionation reaction:



Identify the oxidised product.

- c. What is the equivalent weight of $\text{K}_2\text{S}_2\text{O}_3$ in the reaction with I_2 in acidic medium?

3. a. What is the equivalent weight of H_3PO_2 when it disproportionates into PH_3 and H_3PO_3 ?

- b. What is the equivalent weight of H_3PO_2 when it acts as an acid?

ANSWERS

Subjective Type

1. a. 106.66 b. 271 c. 178.5 d. 20.42

2. a. (i) 46.8, 117 (ii) 53.83, 107.6

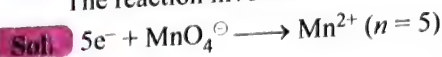
b. ClO_3^- c. 190

3. a. 49.5 b. 66

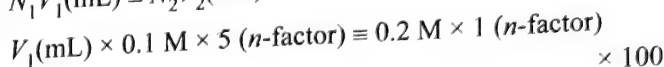
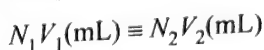
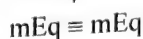
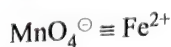
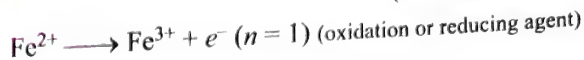
Illustrations of the Concept

1. What volume of 0.1 M KMnO_4 is required to oxidise 100 mL of 0.2 M FeSO_4 in acidic medium?

The reaction involved is



(reduction or oxidising agent)

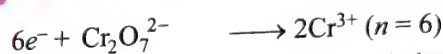


$$0.5 V_1 \equiv 0.2 \times 100$$

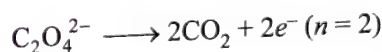
$$V_1 \equiv 40 \text{ mL}$$

2. What volume of 0.2 M $\text{K}_2\text{Cr}_2\text{O}_7$ is required to oxidise 50 mL of 0.3 M $\text{Na}_2\text{C}_2\text{O}_4$ in acidic medium?

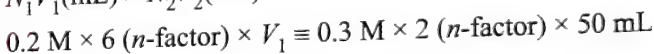
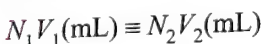
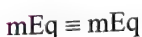
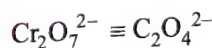
Sol. The reaction involved is



(reduction or oxidising agent)



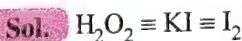
(oxidation or reducing agent)



$$1.2 V_1 \equiv 0.6 \times 50$$

$$V_1 \equiv 25 \text{ mL}$$

3. 5 mL solution of H_2O_2 liberates 1.27 g of iodine from an acidified KI solution. What is the molarity of H_2O_2 ?

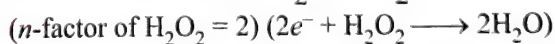


$$N_1 \times V_1 \equiv \frac{\text{Weight of } \text{I}_2}{\text{Ew}(\text{I}_2)} \times 10^3 \text{ mEq}$$

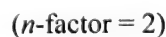
$$N_1 \times 5 \text{ mL} \equiv \frac{1.27 \times 10^3}{\frac{127 \times 2}{2}} \text{ (} n\text{-factor of } \text{I}_2 = 2 \text{)}$$

$$\text{Normality of } \text{H}_2\text{O}_2 \equiv 2 \text{ N}$$

$$\text{Molarity of } \text{H}_2\text{O}_2 \equiv \frac{\text{Normality}}{2} = \frac{2}{2} = 1 \text{ M}$$



4. How many moles of KMnO_4 will be required to react completely with 1 mol of $\text{K}_2\text{C}_2\text{O}_4$ (potassium oxalate) in acidic medium?



$$\frac{1}{5} \text{ mol} \equiv \frac{1}{2} \text{ mol}$$

$$\therefore 1 \text{ mol of } \text{C}_2\text{O}_4^{2-} = \frac{2}{5} \text{ mol of } \text{MnO}_4^-$$

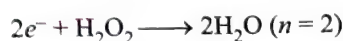
5. How many moles of H_2O_2 will be required to react completely with 1.5 mol of $\text{K}[\text{Cr}(\text{OH})_4]$ (potassium tetrahydroxochromate (I)) in basic medium?

Sol. $[\text{Cr}(\text{OH})_4]^\ominus$ is oxidised to CrO_4^{2-} (chromate) ion.



$$x - 4 = -1 \quad x - 8 = -2$$

$$x = 3 \quad x = 6$$

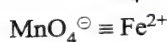
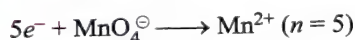
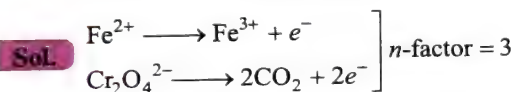


$$(n\text{-factor} = 3) \quad (n\text{-factor} = 2)$$

$$1 \text{ mol of } [\text{Cr}(\text{OH})_4]^\ominus \equiv \frac{3}{2} \text{ mol of } \text{H}_2\text{O}_2$$

$$1.5 \text{ mol of } [\text{Cr}(\text{OH})_4]^\ominus \equiv \frac{3}{2} \times 1.5 = \frac{9}{4} \text{ mol of } \text{H}_2\text{O}_2$$

6. What volume of 0.1 M KMnO_4 is required to oxidise 100 mL of 0.3 M FeC_2O_4 (ferrous oxalate) in acidic medium?



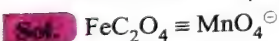
$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

$$N_1 V_1 (\text{mL}) \equiv N_2 V_2 (\text{mL})$$

$$0.1 \times 5 (n\text{-factor}) \times V_1 \equiv 0.3 \times 3 (n\text{-factor}) \times 100 \text{ mL}$$

$$V_1 = \frac{0.3 \times 3 \times 100}{0.1 \times 5} = 180 \text{ mL}$$

7. How many moles of FeC_2O_4 are required to reduce 2 mol of KMnO_4 in acidic medium?



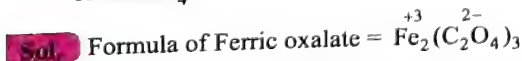
$$1 \text{ Eq} \equiv 1 \text{ Eq}$$

$$\frac{1}{3} \text{ mol} \equiv \frac{1}{5} \text{ mol}$$

$$1 \text{ mol of } \text{KMnO}_4 = \frac{5}{3} \text{ mol of } \text{FeC}_2\text{O}_4$$

$$2 \text{ mol of } \text{KMnO}_4 = \frac{10}{3} \text{ mol of } \text{FeC}_2\text{O}_4$$

8. 100 mL of x M KMnO_4 is required to oxidise 200 mL of 0.2 M ferric oxalate in acidic medium. What is the normality of KMnO_4 ?



Fe^{3+} ion does not oxidise, whereas $\text{C}_2\text{O}_4^{2-}$ ion oxidises to CO_2 .



$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

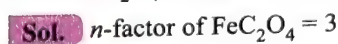
$$N_1 V_1 (\text{mL}) \equiv N_2 V_2 (\text{mL})$$

$$x \times 5 (n\text{-factor}) \times 100 \text{ mL} = 0.2 \times 6 (n\text{-factor}) \times 200 \text{ mL}$$

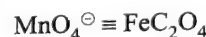
$$x = \frac{0.2 \times 6 \times 200}{5 \times 100} = \frac{24}{50} \text{ M}$$

$$\text{Normality} = n \times M = 5 \times \frac{24}{50} = 2.4 \text{ N}$$

9. What volume of 0.2 N KMnO_4 is required to oxidise 10 mg of ferrous oxalate in acidic medium? (Molecular weight of FeC_2O_4 is 144 g)



(Since normality of MnO_4^- is given, so $n\text{-factor of } \text{MnO}_4^-$ is not required)



$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

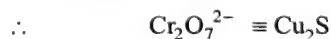
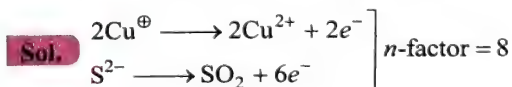
$$N_1 V_1 (\text{mL}) \equiv \frac{\text{Weight}}{\text{Equivalent weight}} \times 10^3 (\text{mEq})$$

$$0.2 \text{ N} \times V_1 (\text{mL}) = \frac{10 \times 10^{-3} \text{ g} \times 10^3}{\frac{144}{3}}$$

$$V_1 = \frac{10 \times 3}{144 \times 0.2} = \frac{300}{288} = 1.04 \text{ mL}$$

$$\text{Volume of } \text{KMnO}_4 = 1.04 \text{ mL}$$

10. What volume of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ is required to oxidise 50 mL of 0.2 M Cu_2S (cuprous sulphide) in acidic medium to give Cr^{3+} , Cu^{2+} , and $\text{SO}_2(\text{g})$?



$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

$$N_1 V_1 (\text{mL}) \equiv N_2 V_2 (\text{mL})$$

$$0.1 \times 6 (n\text{-factor}) \times V_1 \equiv 0.2 \times 8 (n\text{-factor}) \times 50 \text{ mL}$$

$$V_1 = \frac{0.2 \times 8 \times 50}{0.1 \times 6} = 133.33 \text{ mL}$$

11. How many moles of $\text{K}_2\text{Cr}_2\text{O}_7$ are required to react completely with 2.5 mol of Cu_2S in acidic medium?



$$1 \text{ Eq} \equiv 1 \text{ Eq}$$

$$\frac{1}{6} \text{ mol} \equiv \frac{1}{8} \text{ mol}$$

$$1 \text{ mol of Cu}_2\text{S} \equiv \frac{8}{6} \text{ mol of Cr}_2\text{O}_7^{2-}$$

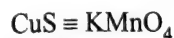
$$2.5 \text{ mol of Cu}_2\text{S} \equiv \frac{2.5 \times 8}{6} = 3.33 \text{ mol}$$

$$\text{Moles of K}_2\text{Cr}_2\text{O}_7 = 3.33 \text{ mol}$$

12. What weight of KMnO_4 is required to react completely with 500 mL of 0.4 M CuS in acidic medium?

Sol. Cu^{2+} is not oxidised but S^{2-} ion is oxidised to SO_2 .
 n -factor = 6). n -factor for $\text{KMnO}_4 = 5$

$$(\text{Mw of KMnO}_4 = 158 \text{ g mol}^{-1})$$



$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

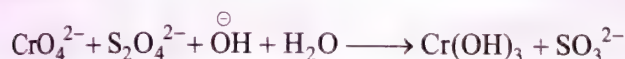
$$N_1 V_1 (\text{mL}) \equiv \frac{\text{Weight}}{\text{Equivalent weight}} \times 10^3 \text{ mEq}$$

$$0.4 \times 6 (n\text{-factor}) \times 500 = \frac{\text{Weight} \times 10^3}{\frac{158}{5}}$$

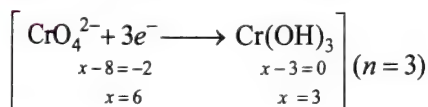
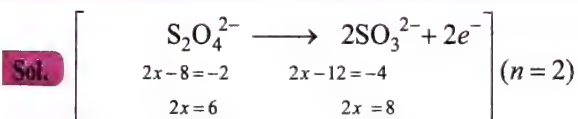
$$\therefore \text{Weight of KMnO}_4 = \frac{0.4 \times 6 \times 500 \times 158}{5 \times 1000} = 37.92 \text{ g}$$

ILLUSTRATION 3.8

In a chrome plating plant, CrO_4^{2-} (chromate) ions are present in waste water. The chromate ions are reduced to insoluble chromium hydroxide, $\text{Cr}(\text{OH})_3$, by dithionate ion, $\text{S}_2\text{O}_4^{2-}$ in basic medium.

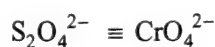


10 L of water requires 522 g of $\text{Na}_2\text{S}_2\text{O}_4$. Calculate the normality and molarity of CrO_4^{2-} in waste water. Also express the concentration of Na_2CrO_4 in ppm.



$$\text{Mw} (\text{Na}_2\text{S}_2\text{O}_4) = 2 \times 23 + 2 \times 32 + 16 \times 4 = 174 \text{ g}$$

$$\left(\text{Ew} = \frac{174}{2} \right)$$



$$\text{Eq} \equiv \text{Eq}$$

$$\frac{\text{Weight}}{\text{Equivalent weight}} \equiv \text{Eq}$$

$$\frac{522}{174} \equiv \text{Eq}$$

$$\frac{2}{2}$$

$$\therefore 6 \text{ Eq of S}_2\text{O}_4^{2-} \equiv \frac{6 \text{ Eq of CrO}_4^{2-}}{10 \text{ L of water}}$$

$$\equiv \frac{6}{10} = 0.6 \text{ Eq L}^{-1}$$

$$\therefore \text{Normality of CrO}_4^{2-} = 0.6 \text{ N}$$

$$\text{Molarity of CrO}_4^{2-} = \frac{N}{n\text{-factor}} = \frac{0.6}{3} = 0.2 \text{ M}$$

$$\text{Strength of Na}_2\text{CrO}_4 = M \times \text{Mw}$$

$$(\text{Mw Na}_2\text{CrO}_4 = 2 \times 23 + 52 + 16 \times 4 = 162 \text{ g})$$

$$= 0.2 \times 162 = 32.4 \text{ g L}^{-1}$$

Concentration in ppm

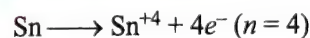
$$= \frac{\text{Weight of Na}_2\text{CrO}_4 \text{ in } 1000 \text{ mL} \times 10^6}{1000 \text{ mL}}$$

$$= \frac{32.4 \times 10^6}{10^3} = 32400 \text{ ppm}$$

ILLUSTRATION 3.9

Metallic tin (Sn) is oxidised to its maximum oxidation state by KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ separately in the presence of HCl . Calculate the ratios of the volumes of decimolar solutions of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ that would be reduced by 1.0 g of Sn (Atomic weight of Sn = 118.6).

Sol. Sn is oxidised to +4 oxidation state (maximum oxidation state of Sn = +4)



$$\text{Equivalent of Sn} = \frac{\text{Weight}}{\text{Ew}} = \frac{1.0}{\frac{118.6}{4}} = \frac{4}{118.6} \text{ Eq}$$



$$\text{Eq} \equiv \text{Eq}$$

$$\frac{4}{118.6} \equiv 0.1 \times 5 (n\text{-factor}) \times V(\text{L})$$

$$V_{\text{MnO}_4^-} = \frac{4}{118.6 \times 0.1 \times 5} = \frac{4}{59.3} = 0.067 \text{ L}$$



$$\text{Eq} \equiv \text{Eq}$$

$$\frac{4}{118.6} \equiv 0.1 \times 6 (n\text{-factor}) \times V(\text{L})$$

$$V_{\text{Cr}_2\text{O}_7^{2-}} = \frac{4}{118.6 \times 0.1 \times 6} = \frac{4}{71.16} = 0.057 \text{ L}$$

Alternatively

$$\frac{V_{\text{MnO}_4^-}}{V_{\text{Cr}_2\text{O}_7^{2-}}} = \frac{6}{5} = 6.5 \left(\frac{n\text{-factor of Cr}_2\text{O}_7^{2-}}{n\text{-factor of MnO}_4^-} \right)$$

Since the same equivalent of Sn is reacting with 0.1 M of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, the ratios of the volumes of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ reacting with the same equivalent of Sn is inversely proportional to their n -factors.

ILLUSTRATION 3.10

Upon heating 1 L of 2 N HCl solution, 36.5 g of HCl is lost and the volume of solution reduces to 800 mL. Calculate

- The normality of the resultant solution
- The number of equivalents of HCl in 100 mL of the original solution.

Sol. mEq of HCl = $N \times V(\text{mL}) = 2 \times 1000 = 2000 \text{ mEq}$

$$\frac{W}{E_w} \times 10^3 = 2000$$

$$\frac{W \times 1000}{36.5} = 2000$$

$$W_{\text{HCl}} = 2 \times 36.5$$

a. Since 36.5 g of HCl is lost on heating and volume becomes 800 mL.

$$W_{\text{HCl left}} = 2 \times 36.5 - 36.5 = 36.5 \text{ g}$$

$$\text{mEq of HCl left} = \frac{W \times 10^3}{E_w} = \frac{36.5 \times 1000}{36.5} = 1000 \text{ mEq}$$

Normality of resultant solution

$$= \frac{\text{mEq}}{V(\text{mL})} = \frac{1000}{800} = 1.25 \text{ N}$$

b. mEq of HCl in 1 L of original solution = 2000

$$\begin{aligned} \text{mEq of HCl in 100 mL of original solution} &= 200 \text{ mEq} \\ &= 200 \times 10^{-3} = 0.2 \text{ Eq} \end{aligned}$$

ILLUSTRATION 3.11

How many moles of HgI_4^{2-} will be formed when 2 mol of Hg^{2+} and 2 mol of I^- react according to the following equation?



a. 1 mol b. 0.5 mol c. 0.25 mol d. 2 mol

Sol. b. $\text{Hg}^{2+} \equiv 4\text{I}^- \equiv \text{HgI}_4^{2-}$
1 mol \equiv 4 mol \equiv 1 mol

$$\frac{1}{4} \text{ mol} \equiv \frac{4}{4} \text{ mol} \equiv \frac{1}{4} \text{ mol}$$

$$\frac{2}{4} \text{ mol} \equiv \frac{4 \times 2}{4} \text{ mol} \equiv \frac{2}{4} \text{ mol} \Rightarrow 0.5 \text{ mol}$$

ILLUSTRATION 3.12

80 mL of KMnO_4 solution reacts with 3.4 g of $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in acidic medium. The molarity of the KMnO_4 solution is

a. 0.5 M b. 0.1 M c. 5 M d. 1 M

Sol. b. $M_w [\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$

$$\begin{aligned} &= 2 \times 23 + 2 \times 12 + 4 \times 16 + 2 \times 18 \\ &= 170 \text{ g} \end{aligned}$$



$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

$$80 \times N \equiv \frac{w \times 10^3}{E_w} \text{ mEq} = \frac{3.4 \times 10^3}{170}$$

$$\therefore N(\text{MnO}_4^-) \equiv \frac{3.4 \times 10^3}{\frac{170}{2} \times 80} = 0.5 \text{ N}$$

$$M(\text{MnO}_4^-) \equiv \frac{0.5 \text{ N}}{5} = 0.1 \text{ M}$$

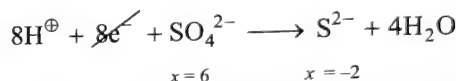
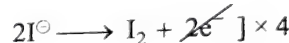
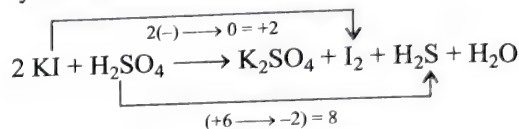
ILLUSTRATION 3.13

KI reacts with H_2SO_4 producing I_2 and H_2S . The volume of 0.2 M H_2SO_4 required to produce 3.4 g of H_2S is

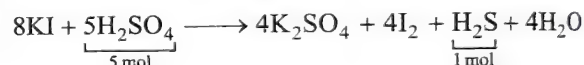
a. 2.5 L b. 3.8 L c. 4 L d. 5 L

Sol.

a. Since the n -factor of H_2S is not known, the problem is solved by mole concept by balancing the equation



Add other ions, i.e. 2H^+ , 8K^+ , and 4SO_4^{2-} , to both sides to balance the equation. Net redox equation is



$$\text{mol of H}_2\text{S} = \frac{3.4}{34} = 0.1 \text{ mol}$$

$$\text{mol of H}_2\text{SO}_4 = 0.1 \times 5 \text{ mol} = 0.5 \text{ mol}$$

$$\therefore 0.2 \times V = 0.5$$

$$V = 2.5 \text{ L}$$

ILLUSTRATION 3.14

40 mL of 0.5 M Ce^{4+} is required to react completely with 10 mL of 1 M Sn^{2+} to Sn^{4+} . What is the oxidation state of cerium in the reduction product?

Sol. $\text{Ce}^{4+} \equiv \text{Sn}^{2+} (\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + 2e^-) (n = 2)$

$$1 \text{ mEq} \equiv 1 \text{ mEq}$$

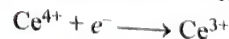
$$N_1 V_1 \equiv N_2 V_2$$

$$0.5 \times n\text{-factor} \times 40 = 1 \times 2 (n\text{-factor}) \times 10$$

$$20n = 20$$

$$n = 1$$

n -factor of Ce^{4+} is 1, i.e., it is reduced to Ce^{3+}

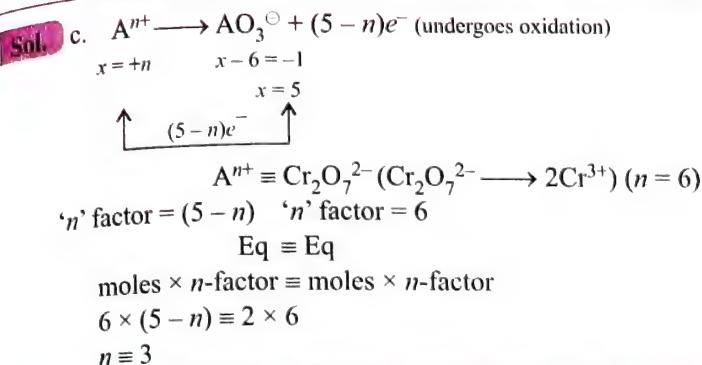


The oxidation state of cerium in the reduction product is +3.

ILLUSTRATION 3.15

6 mol of a solution A^{n+} requires 2 mol of $\text{Cr}_2\text{O}_7^{2-}$ ions for the oxidation of A^{n+} to AO_3^- in acidic medium. The value of n is

a. 1 b. 2 c. 3 d. 4



3.4.7 Mixing of Strong Acids and Strong Bases

- The final concentration of the solution obtained by mixing strong acids is calculated by the formula

$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = N_nV_n$$
 Where $V_n = V_1 + V_2 + V_3 + \dots$
- Similarly, the final concentration of the solution obtained by mixing strong bases is also calculated by the formula.

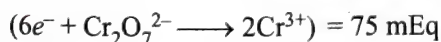
$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = N_nV_n$$
- The final concentration of the solution obtained by mixing strong acids and strong bases can be calculated as follows:
 - Find the total mEq of strong acids and strong bases.
 - Find the mEq of strong acids or strong bases left after neutralisation.
 - Find the concentration of the final solution by dividing the mEq of strong acids or strong bases with the total volume of solution in mL.
- Mixing of solutions of oxidising and reducing agents.
 - Find the total mEq of the oxidising and reducing agents.
 - Find the mEq of the oxidising or reducing agent left after the reaction of the oxidising and reducing agents.
 - Find the concentration of the final solution by dividing the mEq of the oxidising agent or reducing agent left with the total volume of the solution in mL.

ILLUSTRATION 3.16

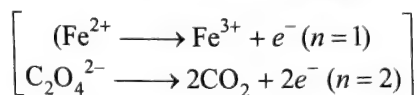
50 mL of an acidic solution of 0.25 M $K_2Cr_2O_7$, 30 mL of 0.4 M $K_2C_2O_4$, and 120 mL of 0.2 M Fe^{2+} are added together. Compute the molarities of Fe^{3+} ions and $Cr_2O_7^{2-}$ ions in the final solution.

Sol.

- a. mEq of oxidising agent ($K_2Cr_2O_7$) (n-factor = 6)
- $$= 50 \times 0.25 \times 6$$



$$\begin{aligned} \text{mEq of reducing agent } (Fe^{2+} + K_2C_2O_4) \\ &= (0.2 \times 120) + (2 \times 0.4 \times 30) \\ &= 24 + 24 = 48 \text{ mEq} \end{aligned}$$



$$Cr_2O_7^{2-} \equiv (Fe^{2+} + C_2O_4^{2-})$$

mEq \equiv mEq

$$75 \text{ mEq} \equiv 48 \text{ mEq}$$

$$\text{Excess mEq of } K_2Cr_2O_7 = 75 - 48 = 27 \text{ mEq}$$

$$\text{Total volume} = 50 + 30 + 120 = 200 \text{ mL}$$

$$\text{Normality of } K_2Cr_2O_7 = \frac{\text{mEq left}}{V(\text{mL})} = \frac{27}{200}$$

$$\text{Molarity of } K_2Cr_2O_7 = \frac{N}{n} = \frac{27}{200 \times 6} = 0.0225 \text{ M}$$

b. mEq of Fe^{3+} produced = mEq of Fe^{2+} reacted
 $= 24 \text{ mEq}$

$$\text{Normality of } Fe^{3+} \text{ produced} = \frac{\text{mEq}}{V \text{ mL}} = \frac{24}{200}$$

$$\text{Molarity of } Fe^{3+} \text{ produced} = \frac{N}{n} = \frac{24}{200 \times 1} = 0.12 \text{ M}$$

ILLUSTRATION 3.17

When 100 mL of 0.06 M $Fe(NO_3)_3$, 50 mL of 0.2 M $FeCl_3$, and 100 mL of 0.26 M $Mg(NO_3)_2$, are mixed. In the final solution

$$\begin{array}{ll} [Fe^{3+}] = \dots\dots & [NO_3^-] = \dots\dots \\ [Cl^-] = \dots\dots & [Mg^{2+}] = \dots\dots \end{array}$$

Sol.

- 100 mL of 0.06 M $Fe(NO_3)_3 \equiv 6 \text{ mmol of } Fe^{3+}$
 $+ 6 \times 3 \text{ mmol of } NO_3^-$
- 50 mL of 0.2 M $FeCl_3 \equiv 10 \text{ mmol of } Fe^{3+}$
 $+ 10 \times 3 \text{ mmol of } Cl^-$
- 100 mL of 0.26 M $Mg(NO_3)_2 \equiv 26 \text{ mmol of } Mg^{2+}$
 $+ 26 \times 2 \text{ mmol of } NO_3^-$
- Total $\equiv 16 \text{ mmol of } Fe^{3+} + 70 \text{ mmol of } NO_3^-$
 $+ 30 \text{ mmol of } Cl^- + 26 \text{ mmol of } Mg^{2+}$

$$\text{Total volume} = 100 + 50 + 100 = 250 \text{ mL}$$

$$[Fe^{3+}] = \frac{16}{250} = 0.064 \text{ M}$$

$$[NO_3^-] = \frac{70}{250} = 0.28 \text{ M}$$

$$[Cl^-] = \frac{30}{250} = 0.12 \text{ M}$$

$$[Mg^{2+}] = \frac{26}{250} = 0.104 \text{ M}$$

ILLUSTRATION 3.18

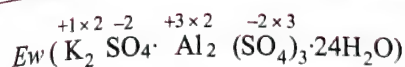
Calculate the concentration of K^+ (x) and Cl^- (y) in a solution obtained by mixing 20 mL of 0.1 M NaCl, 30 mL of 0.2 M KCl, and 25 mL of 0.15 M KNO_3 and making the solution up to 100 mL.

- $x = 0.06, y = 0.0375$
- $x = 0.0975, y = 0.08$
- $x = 0.08, y = 0.06$
- $x = 0.08, y = 0.0375$

Sol.

- b. 1. 20 mL of 0.1 M NaCl $\equiv 2 \text{ mmol of } Na^+$

$$+ 2 \text{ mmol of } Cl^-$$



Total positive or negative charge = 8

$$E_w = \frac{M_w}{8}$$

ILLUSTRATION 3.22

1.0 g of a metal oxide gave 0.2 g of metal. Calculate the equivalent weight of the metal.

Sol. First method: Weight of oxygen = 1.0 – 0.2 = 0.8 g

Let the equivalent weight of metal (M) be E , E_w (oxygen) = 8 g

Equivalent of metal oxide = Equivalent of metal

$$\frac{\text{Weight of Metal oxide}}{E_w(M) + E_w(O)} = \frac{\text{Weight of oxygen}}{E_w(O)}$$

$$\frac{1.0}{E + 8} = \frac{0.8}{8} = 0.1$$

$$0.1(E + 8) = 1.0$$

$$E = 2$$

Second method:

Eq of metal = Eq of oxygen

$$\frac{\text{Weight of M}}{E_w(M)} = \frac{\text{Weight of oxygen}}{E_w(O)}$$

$$\frac{0.2}{E} = \frac{0.8}{8}$$

$$E = 2$$

General formula: If x g of a metal oxide gave y g of metal, then equivalent weight of element is:

$E_w(M)$

$$= \frac{\text{Weight of M}}{\text{Weight of metal oxide} - \text{Weight of M}} \times E_w(\text{Oxygen})$$

$$= \frac{x \times 8}{x - y} = \frac{0.2 \times 8}{1.0 - 0.2} = \frac{0.2 \times 8}{0.8} = 2$$

ILLUSTRATION 3.23

3.0 g of metal chloride gave 2.0 g of metal. Calculate the equivalent weight of the metal.

Sol. Let the equivalent weight of metal (M) be E .

$$E_w(Cl) = 35.5 \text{ g}$$

$$\text{Weight of Cl} = 3.0 - 2.0 = 1.0 \text{ g}$$

Eq of metal = Eq of Cl

$$\frac{\text{Weight of M}}{E_w(M)} = \frac{\text{Weight of Cl}}{E_w(Cl)}$$

$$\frac{2.0}{E} = \frac{1.0}{35.5}$$

$$E = 71.0 \text{ g}$$

General formula: If x g of a metal chloride gave y g of metal, the E_w of metal is

E_w of M

$$= \frac{\text{Weight of M}}{\text{Weight of M chloride} - \text{Weight of M}} \times E_w(Cl)$$

$$= \frac{x \times 35.5}{x - y} = \frac{2.0 \times 35.5}{(3.0 - 2.0)} = 71.0 \text{ g}$$

ILLUSTRATION 3.24

1.0 g of metal nitrate gave 0.86 g of metal sulphate. Calculate the equivalent weight of metal.

Sol. $E_w(NO_3^{(-)}) = \frac{M_w(NO_3^{(-)})}{\text{Charge}} = \frac{14 + 3 \times 16}{1} = 62$

$$E_w(SO_4^{2-}) = \frac{M_w(SO_4^{2-})}{\text{Charge}} = \frac{32 + 4 \times 16}{2} = \frac{96}{2} = 48$$

Equivalent of metal nitrate = Equivalent of metal sulphate

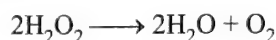
$$\frac{\text{Weight of metal nitrate}}{E_w(M) + E_w(NO_3^{(-)})} = \frac{\text{Weight of metal Sulphate}}{E_w(M) + E_w(SO_4^{2-})}$$

$$\frac{1.0}{E + 62} = \frac{0.86}{E + 48}$$

$$\therefore E = 38$$

3.5 VOLUME STRENGTH OF H_2O_2

It is the volume of O_2 given out at STP on heating 1 N H_2O_2 solution. It is also called the strength of H_2O_2 in terms of available oxygen.



$$2 \text{ mol} \qquad 1 \text{ mol}$$

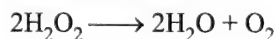
$$2 \text{ mol of } H_2O_2 \equiv 22.4 \text{ L of } O_2$$

$$1 \text{ mol of } H_2O_2 \equiv 11.2 \text{ L of } O_2$$

$$1 \text{ M } H_2O_2 \equiv 11.2 \text{ L of } O_2$$

$$1 \text{ N } H_2O_2 \equiv 5.6 \text{ L of } O_2 \equiv 5.6 \text{ volume of } O_2$$

Alternatively:



$$2 \times 34 \text{ g L}^{-1} \equiv 22.4 \text{ L of } O_2 \text{ at STP}$$

$$17 \text{ g L}^{-1} \equiv 1 \text{ N} \equiv 5.6 \text{ L of } O_2$$

Alternatively:

$$H_2O_2 \equiv O_2$$

$$1 \text{ Eq} \equiv 1 \text{ Eq} \left(\frac{22.4}{4} \text{ L} = 5.6 \text{ L} \right)$$

$$1.7\% \text{ of } H_2O_2 \equiv 17 \text{ g L}^{-1} \text{ of } H_2O_2 \equiv 1 \text{ N} \equiv 5.6 \text{ L of } O_2 \text{ at STP} \equiv 8 \text{ g of } O_2$$

$$(1 \text{ L} \equiv 1000 \text{ mL of } H_2O_2 \equiv 17 \text{ g of } H_2O_2)$$

$$100 \text{ mL of } H_2O_2 \equiv 1.7 \text{ g of } H_2O_2 \equiv 1.7\% \text{ of } H_2O_2$$

General formula of volume strength of H_2O_2

a. $1.7\% \text{ of } H_2O_2 \equiv 17 \text{ g L}^{-1} \text{ of } H_2O_2 \equiv 5.6 \text{ L of } O_2 \text{ at STP} \equiv 8 \text{ g of } O_2 \text{ at STP}$

b. Volume strength of $H_2O_2 \times \text{volume of } H_2O_2 = \text{Volume of } O_2 \text{ at STP}$

- c. 3% solution of H_2O_2 is marked as 10 volume H_2O_2
 d. 30% solution of H_2O_2 is marked as 100 volume H_2O_2

ILLUSTRATION 3.25

Calculate (a) normality, (b) molarity, (c) strength in g L^{-1} , and (d) percentage strength of 10 volume strength of H_2O_2 .

Sol.

- a. '5.6' volume strength of $\text{H}_2\text{O}_2 \equiv 1\text{N}$
 10 volume strength of $\text{H}_2\text{O}_2 = \frac{10}{5.6} \text{N} = 1.785 \text{N}$
 b. $M = \frac{N}{n\text{-factor}} = \frac{1.785}{2}$ ($n\text{-factor of } \text{H}_2\text{O}_2 = 2$)
 $= 0.89 \text{M}$
 c. 5.6 volume strength of $\text{H}_2\text{O}_2 = 17 \text{ g L}^{-1}$
 10 volume strength of $\text{H}_2\text{O}_2 = \frac{17 \times 10}{5.6} = 30.35 \text{ g L}^{-1}$
 d. 5.6 volume strength (or volume) of $\text{H}_2\text{O}_2 = 1.7\%$
 10 volume strength of $\text{H}_2\text{O}_2 = \frac{1.7 \times 10}{5.6} = 3.03\%$

ILLUSTRATION 3.26

Calculate the number of moles and weight of O_2 produced on heating 1.12 L of 10 volume strength of H_2O_2 at STP.

Sol. Volume of O_2 at STP = Volume of $\text{H}_2\text{O}_2 \times$ Volume strength of H_2O_2

$$= 1.12 \text{ L} \times 10 = 11.2 \text{ L}$$

$$\text{Moles of } \text{O}_2 \text{ at STP} = \frac{11.2 \text{ L}}{22.4 \text{ L}} = 0.5 \text{ mol}$$

$$\text{Weight of } \text{O}_2 = 0.5 \times 32 = 16.0 \text{ g}$$

ILLUSTRATION 3.27

0 mL of H_2O_2 liberates 12.7 g of iodine from an acidic KI solution. Calculate the (a) normality, (b) molarity, (c) volume strength, (d) strength, and (e) percentage strength of H_2O_2 .

Sol.

a. $Mw(\text{I}_2) = 2 \times 127 = 254 \text{ g}$

$$Ew(\text{I}_2) = \frac{254}{2} = 127 \text{ g} \quad (2\text{I}^\ominus \rightarrow \text{I}_2 + 2\text{e}^-) (n = 2)$$

$$\text{H}_2\text{O}_2 \equiv \text{KI} \equiv \text{I}_2$$

$$1 \text{ mEq} \equiv 1 \text{ mEq} \equiv 1 \text{ mEq}$$

$$N_1 V_1 (\text{mL}) \equiv \frac{\text{Weight of } \text{I}_2}{Ew(\text{I}_2)} \times 10^3 (\text{mEq})$$

$$N_1 \times 10 \text{ mL} \equiv \frac{12.7 \times 10^3}{127}$$

$$N_1 \text{ of } \text{H}_2\text{O}_2 \equiv 10 \text{ N}$$

b. $\text{Molarity of } \text{H}_2\text{O}_2 = \frac{N}{n\text{-factor}} = \frac{10}{2} = 5 \text{ M}$

- c. 1 N of $\text{H}_2\text{O}_2 = 5.6$ volume of H_2O_2 .
 10 N of $\text{H}_2\text{O}_2 = 56$ volume strength of H_2O_2
 d. 1 N of $\text{H}_2\text{O}_2 = 17 \text{ g L}^{-1}$
 10 N of $\text{H}_2\text{O}_2 = 170 \text{ g L}^{-1}$
 e. 1 N of $\text{H}_2\text{O}_2 = 1.7\%$
 10 N of $\text{H}_2\text{O}_2 = 17\%$

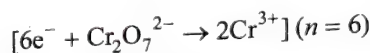
ILLUSTRATION 3.28

A solution of $\text{K}_2\text{Cr}_2\text{O}_7$ containing 4.9 g L^{-1} is used to titrate H_2O_2 solution containing 3.4 g L^{-1} in acidic medium. What volume of $\text{K}_2\text{Cr}_2\text{O}_7$ will be required to react with 20 mL of H_2O_2 solution? Also calculate the strength of H_2O_2 in terms of available oxygen.

Sol. Strength = $N \times Ew$

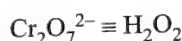
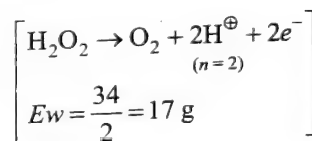
$$Ew(\text{K}_2\text{Cr}_2\text{O}_7) = \frac{39 \times 2 + 52 \times 2 + 16 \times 7}{6}$$

$$= \frac{294}{6} = 49.0 \text{ g}$$



$$N(\text{K}_2\text{Cr}_2\text{O}_7) = \frac{\text{Strength}}{Ew} = \frac{4.9}{49} = 0.1 \text{ N}$$

$$N(\text{H}_2\text{O}_2) = \frac{\text{Strength}}{Ew} = \frac{3.4}{17} = 0.2 \text{ N}$$



$$\text{mEq} \equiv \text{mEq}$$

$$N_1 V_1 \equiv N_2 V_2$$

$$0.1 \times V_1 = 0.2 \times 20$$

$$V_1 = \frac{0.2 \times 20}{0.1} = 40 \text{ mL}$$

Volume strength of H_2O_2 :

$$1 \text{ N} = 5.6 \text{ L of } \text{O}_2 \text{ (volume strength of } \text{H}_2\text{O}_2)$$

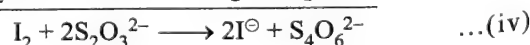
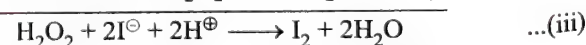
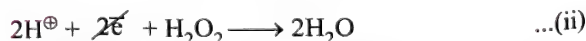
$$0.2 \text{ N} = 5.6 \times 0.2 = 1.12 \text{ L of } \text{H}_2\text{O}_2$$

It is written as 1.12 volume H_2O_2 .

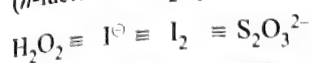
ILLUSTRATION 3.29

When 100 mL of an aqueous solution of H_2O_2 is titrated with an excess of KI solution in dilute H_2SO_4 , the liberated I_2 required 50 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reaction. Calculate the percentage strength and volume strength of H_2O_2 solution.

Sol. Reactions involved are as follows:



(n -factor for $2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$ is $\frac{2}{2} = 1$).



$$\text{mEq} \equiv \text{mEq} \equiv \text{mEq} \equiv \text{mEq}$$

$$N_1 V_1 (\text{mL}) \equiv N_2 V_2 (\text{mL})$$

$$N_1 \times 100 \equiv 0.1 \times 1 \text{ (} n\text{-factor) } \times 50 \text{ mL}$$

$$N(\text{H}_2\text{O}_2) = \frac{0.1 \times 1 \times 50}{100} = 0.05 \text{ N}$$

$$1 \text{ N H}_2\text{O}_2 \equiv 1.7\% \text{ of H}_2\text{O}_2$$

$$0.05 \text{ N H}_2\text{O}_2 \equiv 1.7 \times 0.05 = 0.085 \%$$

$$\text{Percentage strength of H}_2\text{O}_2 = 0.085\%$$

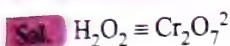
$$1 \text{ N H}_2\text{O}_2 \equiv 5.6 \text{ volume of O}_2$$

$$0.05 \text{ N H}_2\text{O}_2 \equiv 5.6 \times 0.05 = 0.28 \text{ volume of O}_2$$

$$\text{Volume strength of H}_2\text{O}_2 \text{ solution} = 0.28 \text{ volume}$$

ILLUSTRATION 3.30

Calculate the volume strength of H_2O_2 solution if 50 mL of H_2O_2 solution is diluted with 50 mL of H_2O . 20 mL of this diluted solution required 40 mL of $\text{M}/60 \text{ K}_2\text{Cr}_2\text{O}_7$ solution in presence of H_2SO_4 for complete reaction.



$$(n = 2) \quad (n = 6)$$

$$\text{mEq} \equiv \text{mEq}$$

$$N_1 V_1 \equiv N_2 V_2$$

$$N_1 \times 20 \equiv \frac{1}{60} \times 6 \times 40$$

$$N(\text{H}_2\text{O}_2) = \frac{4}{20} = 0.2 \text{ N}$$

The normality of the 50 mL of H_2O_2 should be twice the normality of 20 mL of the diluted solution of H_2O_2 , since the volume of H_2O_2 solution has doubled.

(50 mL of H_2O_2 + 50 mL of H_2O = 100 mL of solution of H_2O_2)

$$\therefore N(\text{H}_2\text{O}_2) \text{ of 50 mL of H}_2\text{O}_2 = 0.2 \times 2 = 0.4 \text{ N}$$

$$\therefore \text{Volume strength of H}_2\text{O}_2 = 5.6 \times 0.4 = 2.24 \text{ volume of O}_2$$

ILLUSTRATION 3.31

50 mL of ozone (O_3) at STP were passed through 50 mL of '5 volume' H_2O_2 solution. What is the volume strength of H_2O_2 after the reaction?



$$(1/2 \text{ vol}) \quad (1/2 \text{ vol}) \quad (1 \text{ vol})$$

From Eqs. (i) and (ii), we get 50 mL of O_3 at STP will produce 50 mL of molecular O_2 as such and 50 mL of oxygen molecule after reaction with H_2O_2 .

This new volume of 50 mL of molecular oxygen after reaction with H_2O_2 is contributed equally by O_3 and H_2O_2 .

Thus, 25 mL of oxygen has been contributed by H_2O_2 .

Volume of $\text{H}_2\text{O}_2 \times$ Volume strength of H_2O_2 = Volume of O_2 at STP

$$50 \text{ mL} \times 5 \text{ V H}_2\text{O}_2 = 250 \text{ mL of O}_2 \text{ at STP}$$

After utilisation of 25 mL of O_2 , according to equation (iii),

The balance $(250 - 25) = 225 \text{ mL of O}_2$ at STP are still available by 50 mL of H_2O_2 .

Hence, volume strength of H_2O_2 after reaction is

$$\frac{\text{Volume of O}_2 \text{ at STP}}{\text{Volume of H}_2\text{O}_2} = \frac{225}{50} \quad m = 4.5$$

$$\therefore \text{Volume strength} = 4.5$$

ILLUSTRATION 3.32

5.1 g sample of H_2O_2 solution containing $x\%$ H_2O_2 by weight requires x mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution for complete oxidation under acidic condition. What is the molarity of $\text{K}_2\text{Cr}_2\text{O}_7$ solution?

Sol. 100 g of H_2O_2 solution contains x g of H_2O_2

$$5.1 \text{ g of H}_2\text{O}_2 \text{ solution contains } \frac{x \times 5.1}{100}$$

$$= \text{Weight of H}_2\text{O}_2$$

$$\text{mEq of H}_2\text{O}_2 = \frac{\text{Weight of H}_2\text{O}_2 \times 10^3}{\text{Ew H}_2\text{O}_2}$$

$$= \frac{5.1x}{100} \times \frac{1}{17} \times 10^3 = 3x \text{ mEq}$$

$$\therefore \text{Cr}_2\text{O}_7^{2-} \equiv \text{H}_2\text{O}_2$$

$$\text{mEq} \equiv \text{mEq}$$

$$N_1 V_1 (\text{mL}) \equiv 3x$$

$$N_1 \times x \text{ mL} = 3x$$

$$N(\text{K}_2\text{Cr}_2\text{O}_7) = 3 \text{ N}$$

$$M(\text{K}_2\text{Cr}_2\text{O}_7) = \frac{N}{n} = 0.5 \text{ M}$$

ILLUSTRATION 3.33

200 mL of acidified 3 N H_2O_2 is reacted with KMnO_4 solution till there is a light tinge of purple colour. Calculate the volume of O_2 produced at STP.

Sol. 1 N of H_2O_2 = 5.6 volume of O_2

$$3 \text{ N of H}_2\text{O}_2 = 3 \times 5.6 = 16.8 \text{ volume of O}_2 \text{ (volume strength of H}_2\text{O}_2)$$

$$\text{Volume of O}_2 \text{ produced by H}_2\text{O}_2 \text{ at STP}$$

$$= \text{Volume of O}_2 \times \text{Volume strength of H}_2\text{O}_2$$

$$= 200 \text{ mL} \times 16.8 = 3360 \text{ mL}$$

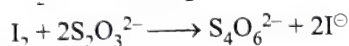
$$\text{Same volume will be produced by KMnO}_4 = 3360 \text{ mL}$$

$$\text{Total volume of O}_2 = 3360 + 3360 = 6720 \text{ mL} = 6.72 \text{ L}$$

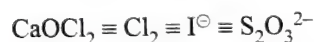
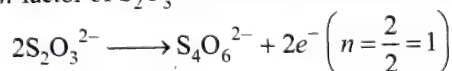
3.6 STRENGTH OF BLEACHING POWDER (CaOCl₂) IN TERMS OF PERCENTAGE OF AVAILABLE CHLORINE FROM THE SAMPLE OF BLEACHING POWDER

When bleaching powder solution is heated, it liberates Cl₂. The liberated Cl₂ is titrated with KI solution which gives I₂. I₂ is titrated with Na₂S₂O₃ (sodium thiosulphate) solution, which gives the percentage of available chlorine.

Reactions involved are as follows:



n-factor of S₂O₃²⁻ in acidic medium is one.

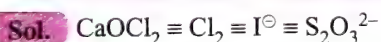


$$\text{mEq} \equiv \text{mEq} \equiv \text{mEq} \equiv \text{mEq}$$

From the mEq of S₂O₃²⁻, the mEq and weight of Cl₂ can be determined. Then percentage of available Cl₂ is determined.

ILLUSTRATION 3.34

0.71 g of a sample of bleaching powder (CaOCl₂) is dissolved in 100 mL of water. 50 mL of this solution is titrated with KI solution. The I₂ so liberated required 10 mL 0.1 M Na₂S₂O₃ (hypo) solution in acidic medium for complete neutralisation. Calculate the percentage of available Cl₂ from the sample of bleaching powder.



$$\text{mEq} \equiv \text{mEq} \equiv \text{mEq} \equiv \text{mEq}$$

$$\text{mEq} \equiv \text{mEq} \equiv \text{mEq} \equiv \text{mEq}$$

$$- \equiv - \equiv - \equiv 10 \text{ mL} \times 0.1 \times 1 \text{ (} n\text{-factor)}$$

$$- \equiv 1 \text{ mEq} \equiv 1 \text{ mEq}$$

$$\text{Thus mEq of Cl}_2 \text{ in 50 mL of solution} = 1 \text{ mEq}$$

$$\text{mEq of Cl}_2 \text{ in 100 mL of solution} = 1 \times 2 = 2 \text{ mEq}$$

$$\text{Weight of Cl}_2 = \text{mEq} \times 10^{-3} \times Ew(\text{Cl}_2)$$

$$= 2 \times 10^{-3} \times \frac{71}{2} \left(n\text{-factor for Cl}_2 = 2 \right)$$

$$\left(\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^- \right)$$

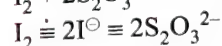
$$= 0.071 \text{ g}$$

$$\% \text{ of available Cl}_2 = \frac{\text{Weight of Cl}_2}{\text{Weight of CaOCl}_2} \times 100$$

$$= \frac{0.071 \times 100}{0.71} = 10\%$$

3.7 IODIMETRIC AND IODOMETRIC TITRATIONS

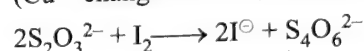
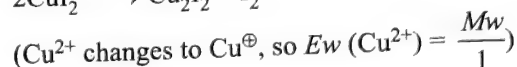
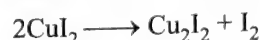
Iodimetry: The estimation of reducing substance by the use of standard I₂ is called iodimetry.



$$Ew(\text{S}_2\text{O}_3^{2-}) = \frac{Mw}{1} \quad (\because 'n' \text{ factor} = \frac{2}{2} = 1)$$

$$Ew(\text{I}_2) = \frac{Mw}{2} \quad (n = 2)$$

Iodometry: The estimation of oxidising substance involving the liberation of I₂ and subsequent volumetric estimation of I₂ is called iodometry.



Starch is used as an indicator near the end point, which forms a blue-coloured complex with I₃⁻. The blue colour disappears when there is no more free I₂.

Alternatively

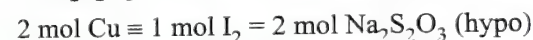
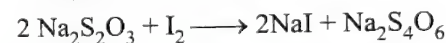
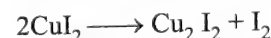
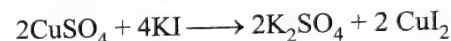
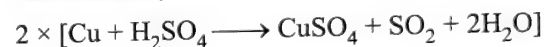


ILLUSTRATION 3.35

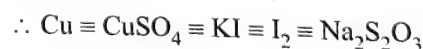
0.5 g sample of copper ore is converted into CuSO₄ solution. The resulting solution is acidified with dilute CH₃COOH (acetic acid) and excess KI added. The liberated I₂ requires 0.248 g Na₂S₂O₃·5H₂O for complete reaction. Calculate the percentage of Cu in the ore.

Sol.

$$Mw(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) = 248 \text{ g}$$

$$Ew = \frac{248}{1} \quad (n = 1)$$

$$Ew(\text{CuSO}_4 \text{ or Cu}) = \frac{M}{1}$$



$$\equiv \frac{0.248}{248} = 10^{-3} \text{ Eq}$$

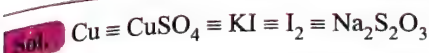
$$\therefore \text{Eq of Cu} = 10^{-3} \text{ Eq}$$

$$\text{Weight of Cu} = \text{Eq} \times Ew = 10^{-3} \times \frac{63.5}{1} \text{ g } (n = 1)$$

$$\% \text{ of Cu} = \frac{63.5 \times 10^{-3} \text{ g} \times 100}{0.5 \text{ g}} = \frac{635 \times 100}{1000 \times 5} = 12.7\%$$

ILLUSTRATION 3.36

50.0 g sample of brass is dissolved in 1L dil H₂SO₄. 20 mL of this solution is mixed with KI, and the liberated I₂ required 20 mL of 0.5 M hypo solution for titration. Calculate the amount of Cu in the alloy.



$$\text{mEq} \equiv \text{mEq} \equiv \text{mEq} \equiv \text{mEq} \equiv \text{mEq}$$

$$? \equiv \text{---} \equiv \text{---} \equiv 20 \times 0.5 \times 1 \quad (n = 1)$$

$$= \frac{10 \text{ mEq of Na}_2\text{S}_2\text{O}_3}{20 \text{ mL of solution}}$$

$$\equiv \frac{10 \times 1000}{20} \text{ mEq L}^{-1} = 500 \text{ mEq L}^{-1} \text{ of solution}$$

$$\text{mEq of Cu in 1 L of solution} \equiv 500 \equiv 500 \times 10^{-3} \text{ Eq}$$

$$\text{Weight of Cu} = 500 \times 10^{-3} \times \frac{63.5}{1} \quad (n\text{-factor} = 1)$$

$$= \frac{635 \times 5}{100} = 31.75 \text{ g}$$

$$\therefore \% \text{ Cu} = \frac{31.75}{50} \times 100 = 63.5\%$$

CONCEPT APPLICATION EXERCISE 3.3

Subjective Type

- Calculate the number of moles of $\text{Cr}_2\text{O}_7^{2-}$ required to oxidise 1 mol of $\text{Fe}(\text{HC}_2\text{O}_4)_2$ in acidic medium. How many moles of NaOH are required to react with 1 mol of $\text{Fe}(\text{HC}_2\text{O}_4)_2$?
- How many moles of NO_2^\ominus are oxidised to NO_3^\ominus by 2 mol of MnO_4^\ominus in dilute basic medium?
- What is the ratio of moles of MnO_4^\ominus used per mol of $\text{C}_2\text{O}_4^{2-}$ in acidic medium to strong basic medium?
- What is the ratio of FeC_2O_4 (ferrous oxalate) and ferric oxalate used per mol of $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium?
- Gastric juice contains 3.65 g of HCl per litre. If a person produces 2.0 L, of gastric juice per day how many antacid tablets, each containing 520 mg of $\text{Al}(\text{OH})_3$, are needed to neutralise all the HCl produced in one day?
- 100 mL of each three samples of H_2O_2 labelled 2.8 vol, 5.6 vol, and 22.4 vol are mixed and then diluted with an equal volume of water. Calculate the volume strength of the resultant H_2O_2 solution.
- 10.0 g of CaOCl_2 is dissolved in water to make 200 mL solution. 20 mL of it is acidified with acetic acid and treated with KI solution. The I_2 liberated required 40 mL of M/20 $\text{Na}_2\text{S}_2\text{O}_3$ solution. Find the percentage of available chlorine.

ANSWERS

Subjective Type

1. $\frac{5}{6}, \frac{1}{2}$ 2. 3 3. 1:5 4. 2:1
5. 10 6. ≈ 5 Vol 7. 7.1%

3.7.1 Titration of Mixture of Compounds with Acid/Base or Oxidising/Reducing Agent

- When a mixture containing two or more compounds is reacted/titrated with acid/base or oxidising agent/reducing agent, the total Eq/mEq of reacting or titrating species is equal to the mEq of both the compounds, when both compounds react with the titrating reagent, for example

when a mixture of Na_2CO_3 and K_2CO_3 is reacted with HCl, in which both Na_2CO_3 and K_2CO_3 react then $\text{mEq of Na}_2\text{CO}_3 + \text{mEq of K}_2\text{CO}_3 = \text{mEq of HCl reacted}$.

- When a mixture containing two or more compounds, in which only one compound reacts with titrating reagent, then the total Eq/mEq of the reacting/titrating reagent is equal to the mEq of the compound which reacts. For example
When mixture of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ is reacted with oxidising agent such as KMnO_4 , or $\text{K}_2\text{Cr}_2\text{O}_7$, only FeSO_4 reacts

$$\text{mEq of FeSO}_4 = \text{mEq of oxidising agent}$$

- Salts formed by the reaction between a strong acid (HCl, H_2SO_4 , HNO_3 , H_3PO_4 , etc) and a strong base NaOH, KOH, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$) when dissolved in water does not affect the acidity or basicity of the solution.

For example: a solution having Na_2SO_4 (formed by the reaction between NaOH and H_2SO_4) as its solute is neutral as Na_2SO_4 is a salt of strong acid and strong base.

- Back titration:** This concept comes into picture while analysing the neutralisation in case any of the acids or bases is found to be in excess (overstepping of the end point).

ILLUSTRATION 3.37

0.5 g of fuming sulphuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$), called oleum, is diluted with water. This solution completely neutralised 26.7 mL of 0.4 M NaOH. Find the percentage of free SO_3 in the sample solution.

Sol. $E_w(\text{SO}_3) = \frac{80}{2} = 40 \text{ g} [\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4, (n = 2)]$

$$E_w \text{ of } \text{H}_2\text{SO}_4 = \frac{98}{2} = 49 \text{ g}$$

Let x g of SO_3 and $(0.5 - x)$ g of H_2SO_4 be present

$$\text{mEq of SO}_3 + \text{mEq of H}_2\text{SO}_4 = \text{mEq of NaOH}$$

$$\left(\frac{x}{40} + \frac{0.5 - x}{49} \right) \times 10^3 \text{ mEq} = 26.7 \times 0.4 \times 1 \text{ mEq}$$

$$\therefore x = 0.103 \text{ g}$$

$$\% \text{ of free SO}_3 = \frac{0.103}{0.5} \times 100 = 20.6\%$$

ILLUSTRATION 3.38

1.84 g of CaCO_3 and MgCO_3 were treated with 50 mL of 0.8 M HCl solution. Calculate the percentage of CaCO_3 and MgCO_3 .

Sol. $E_w(\text{CaCO}_3) = 100/2 = 50 \quad (n = 2)$

$$E_w(\text{MgCO}_3) = 84/2 = 42 \quad (n = 2)$$

Let x g of CaCO_3 and $(1.84 - x)$ g of MgCO_3 be present.

$$\text{mEq of CaCO}_3 + \text{mEq of MgCO}_3 = \text{mEq of HCl}$$

$$\left(\frac{x}{50} + \frac{1.84 - x}{42} \right) \times 10^3 = 50 \times 0.8 \times 1$$

$$\therefore x = 1 \text{ g}$$

$$\% \text{ of CaCO}_3 = \frac{1 \times 100}{1.84} = 54.35\%$$

$$\% \text{ of MgCO}_3 = 100 - 54.35 = 45.65\%$$

ILLUSTRATION 3.39

0.4 g of a mixture containing sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) and potassium oxalate requires 50 mL of $\text{M}/60 \text{ K}_2\text{Cr}_2\text{O}_7$ solution in acidic medium for complete reaction. Calculate the percentage composition of the mixture.

Sol. $\text{Ew}(\text{Na}_2\text{C}_2\text{O}_4) = \frac{2 \times 23 + 2 \times 12 + 4 \times 16}{2} = \frac{134}{2} = 67 \text{ g}$

$\text{Ew}(\text{K}_2\text{C}_2\text{O}_4) = \frac{2 \times 39 + 2 \times 12 + 4 \times 16}{2} = \frac{166}{2} = 83 \text{ g}$

Let $x \text{ g}$ of $\text{Na}_2\text{C}_2\text{O}_4$ and $(0.4 - x) \text{ g}$ of $\text{K}_2\text{C}_2\text{O}_4$ be present.
 $\text{mEq of Na}_2\text{C}_2\text{O}_4 + \text{mEq of K}_2\text{C}_2\text{O}_4 = \text{mEq of K}_2\text{Cr}_2\text{O}_7$

$\left(\frac{x}{67} + \frac{0.4 - x}{83}\right) \times 10^3 = 50 \times \frac{1}{60} \times 6 \text{ (n-factor)}$

$83x + 67(0.4 - x) = \frac{5 \times 67 \times 83}{10^3}$

$16x = 27.8 - 67 \times 0.4$
 $= 27.8 - 26.8 = 1.0$

$x = \frac{1}{16} = 0.06 \text{ g}$

$\% \text{ of Na}_2\text{C}_2\text{O}_4 = \frac{0.06 \times 100}{0.4} = 15.6\%$

$\% \text{ of K}_2\text{C}_2\text{O}_4 = 100 - 15.6 = 84.4\%$

ILLUSTRATION 3.40

2.1 g of a mixture of NaHCO_3 and KClO_3 requires 100 mL of 0.1 N HCl for complete reaction. Calculate the amount of residue that would be obtained on heating 2.2 g of the same mixture strongly.

Sol. $\text{Ew}(\text{NaHCO}_3) = 23 + 1 + 12 + 3 \times 16 = \frac{84}{1} = 84 \text{ (n = 1)}$

HCl reacts only with NaHCO_3 (acid and base reaction)

$\text{mEq of HCl} = 100 \times 0.1$

$= 10 \text{ mEq of NaHCO}_3$

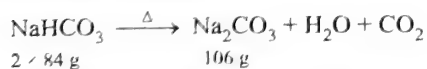
$= 10 \times 10^{-3} \times 84 \text{ g of NaHCO}_3 = 0.84 \text{ g}$

$\text{Weight of KClO}_3 = 2.1 - 0.84 = 1.26 \text{ g}$

$\text{Weight of NaHCO}_3 \text{ in } 2.2 \text{ g of mixture} = \frac{0.84 \times 2.2}{2.1}$
 $= 0.88 \text{ g}$

$\text{Weight of KClO}_3 \text{ in } 2.2 \text{ g of mixture} = (2.2 - 0.88) \text{ g}$
 $= 1.32 \text{ g}$

Heating of mixture:

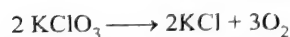


2 \times 84 g

106 g

Weight of residue obtained on heating NaHCO_3

$= \frac{106 \times 0.88}{2 \times 84} = 0.555 \text{ g}$



2 \times 122.5 g 2 \times 74.5 g

Weight of residue obtained on heating KClO_3

$= \frac{2 \times 74.5 \times 1.32}{2 \times 122.5} = 0.802 \text{ g}$

$\text{Total weight of residue} = 0.555 + 0.802 = 1.357 \text{ g}$

ILLUSTRATION 3.41

1.67 g mixture of Al and Zn was completely dissolved in acid and evolved 1.69 L of H_2 at STP. Calculate the weight Al and Zn in the mixture.

Sol. Let x and y be the weights of Al and Zn in the mixture.

$x + y = 1.67$... (i)

$\text{Eq of Al} + \text{Eq of Zn} = \text{Eq of H}_2$

$\left(\frac{a}{27/3} + \frac{b}{65/2}\right) = \frac{1.69}{22.4/2}$... (ii)

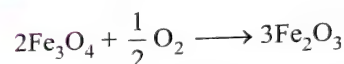
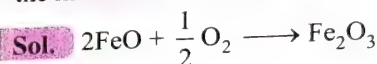
Solving Eqs. (i) and (ii), we get

$x = 1.25 \text{ g}$

$y = 0.42 \text{ g}$

ILLUSTRATION 3.42

A mixture of FeO and Fe_3O_4 when heated in air to constant weights, gains 5% in its weight. Calculate the composition of the mixture.



Let the weights of FeO and Fe_3O_4 be x and $y \text{ g}$, respectively.

$x + y = 100$... (i)

Now, $2 \times 72 \text{ g FeO gives Fe}_2\text{O}_3 = 160 \text{ g}$

$x \text{ g FeO gives Fe}_2\text{O}_3 = \frac{160 \times x}{144} \text{ g}$

Similarly, $2 \times 232 \text{ g of Fe}_3\text{O}_4 \text{ gives Fe}_2\text{O}_3 = 3 \times 160 \text{ g}$

$y \text{ g of Fe}_3\text{O}_4 \text{ gives Fe}_2\text{O}_3 = \frac{3 \times 160 \times y}{464} \text{ g}$

$\therefore \frac{160x}{144} + \frac{3 \times 160 \times y}{464} = 105$... (ii)

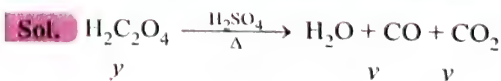
Solving Eqs. (i) and (ii), we get

$x = 20.25 \text{ g} \quad \therefore \text{FeO} = 20.25 \%$

$y = 79.75 \text{ g} \quad \therefore \text{Fe}_3\text{O}_4 = 79.75\%$

ILLUSTRATION 3.43

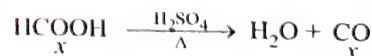
A mixture of $\text{H}_2\text{C}_2\text{O}_4$ and HCOOH is heated with conc H_2SO_4 . The gas produced is collected, and on treatment with KOH solution, the volume of the gas decreases by $\frac{1}{6}$. Calculate the molar ratio of the two acids in the original mixture.



y

y

y



x

x

Let x and y moles of HCOOH and $\text{H}_2\text{C}_2\text{O}_4$ be present in the original mixture.

$\text{Total moles of CO formed} = x + y$

$\text{moles of CO}_2 \text{ formed} = y$

Total moles of gases = $x + y + y = x + 2y$

Since KOH solution absorbs CO_2 and volume reduces by $1/6$,

$$\text{moles of } \text{CO}_2 = \frac{1}{6}(x + 2y)$$

$$y = \frac{1}{6}(x + 2y)$$

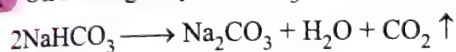
$$\therefore \frac{x}{y} = 4$$

$$\therefore x:y :: 4:1$$

ILLUSTRATION 3.44

2.0 g mixture of Na_2CO_3 , NaHCO_3 , and NaCl on heating produced 56 mL of CO_2 at STP. 1.6 g of the same mixture required 25 mL of 0.5 M H_2SO_4 for complete neutralisation. Calculate the percentage of each component present in the mixture.

Sol. On heating only NaHCO_3 decomposes to give CO_2



Eq of NaHCO_3 = Eq of CO_2

$$\frac{W_{\text{NaHCO}_3}}{E_w(\text{NaHCO}_3)} = \frac{\text{Volume of } \text{CO}_2}{\text{Volume of 1 Eq of } \text{CO}_2}$$

$$\frac{W_{\text{NaHCO}_3}}{84/1} = \frac{56}{22400/2}$$

$$W_{\text{NaHCO}_3} \text{ in 2.0 g of mixture} = \frac{0.42}{2} \times 100$$

$$= 21\% \text{ of mixture}$$

$$\text{Weight of } \text{NaHCO}_3 \text{ in 1.6 of mixture} = \frac{1.6 \times 21}{100} = 0.336 \text{ g}$$

Let the weight of NaCl be x g

$$\text{Weight of } \text{NaHCO}_3 = 0.336 \text{ g}$$

$$\text{Weight of } \text{Na}_2\text{CO}_3 = [1.6 - (x + 0.336)] \text{ g}$$

$$= (1.264 - x) \text{ g}$$

Since both Na_2CO_3 and NaHCO_3 react with H_2SO_4 ,

$$\text{mEq of } \text{Na}_2\text{CO}_3 + \text{mEq of } \text{NaHCO}_3 = \text{mEq of } \text{H}_2\text{SO}_4$$

$$\left(\frac{1.264 - x}{126/2} + \frac{0.336}{84/1} \right) \times 10^3 = 25 \times 0.5 \times 2 \text{ (n-factor)}$$

$$\therefore x = 0.151 \text{ g}$$

$$\therefore \text{Weight of } \text{NaCl} = 0.151 \text{ g and \% of } \text{NaCl} = 9.43\%$$

$$\text{Weight of } \text{NaHCO}_3 = 0.336 \text{ g and \% of } \text{NaHCO}_3 = 21.0\%$$

$$\text{Weight of } \text{Na}_2\text{CO}_3 = 1.264 - 0.151 = 1.113$$

$$\text{and \% of } \text{Na}_2\text{CO}_3 = 69.57\%$$

ILLUSTRATION 3.45

500 mL of 1.0 M $\text{H}_2\text{C}_2\text{O}_4$, 100 mL of 2.0 M H_2SO_4 , and 40 g of NaOH are mixed together. 30 mL of the above mixture is titrated against a standard solution of sodium carbonate containing 14.3 g of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ per 100 mL of solution. Find the volume of carbonate solution used for complete neutralisation.

Sol. $\text{mEq of } \text{H}_2\text{C}_2\text{O}_4 = 2 \times 1.0 \times 500 = 1000$

$$\text{mEq of } \text{H}_2\text{SO}_4 = 2 \times 2.0 \times 100 = 400$$

$$\text{mEq of acid(s)} = 1400$$

$$\text{Now mEq of } \text{NaOH (base)} = \frac{W_t}{E_w} \times 100$$

$$= \frac{40}{40/1} \times 1000 = 1000$$

$$\text{Excess of acid/30 mL in the mixture} = 400$$

$$\text{So mEq of acid} = \text{mEq of carbonate}$$

$$\text{Normality of carbonate} = \frac{\text{Strength}}{E} \frac{143}{286/2}$$

$$(14.3 \text{ g/100 mL} \equiv 143 \text{ g L}^{-1})$$

$$N = 1$$

$$\text{mEq of acid (excess)/30 mL} = \frac{30}{600} \times 400 = 20$$

$$\Rightarrow 20 = NV$$

$$\Rightarrow V = 20 \text{ mL of carbonate}$$

ILLUSTRATION 3.46

Calculate the percentage composition of a solution obtained by mixing 200 g of a 20% and 300 g of a 30% solution by weight.

Sol. Weight of solution I = 200 g

$$\text{Weight of solute in solution I} = \frac{20 \times 200}{100} = 40 \text{ g}$$

$$\text{Weight of solution II} = 300 \text{ g}$$

$$\text{Weight of solute in solution II} = \frac{30 \times 300}{100} = 90 \text{ g}$$

$$\text{Total weight of solute after mixing} = 40 + 90 = 130 \text{ g}$$

$$\text{Total weight of solution after mixing} = 200 + 300 = 500 \text{ g}$$

$$\% \text{ by weight} = \frac{130 \times 100}{500} = 26.0\%$$

ILLUSTRATION 3.47

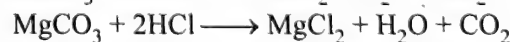
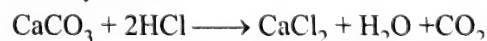
3.75 g of a mixture of CaCO_3 and MgCO_3 is dissolved in 1 L of 0.1 M HCl to liberate 0.04 mol of CO_2 . Calculate

- The percentage of each compound in the mixture
- The amount of acid used
- The amount of acid left after the reaction

Sol.

- Let the weight of CaCO_3 and MgCO_3 be x and y respectively

$$\therefore x + y = 3.75 \quad \dots(i)$$



$$[M_w(\text{CaCO}_3) = 100 \text{ g and } M_w(\text{MgCO}_3) = 84 \text{ g}]$$

$$\text{Mol of } \text{CaCO}_3 + \text{Mol of } \text{MgCO}_3 = \text{Mol of } \text{CO}_2 \text{ formed}$$

$$\therefore \frac{x}{100} + \frac{y}{84} = 0.04$$

$$84x + 100y = 336 \quad \dots(ii)$$

Solving Eqs. (i) and (ii), we get

$$x = 2.4375 \text{ g}$$

$$y = 3.75 - 2.4375 = 1.3125 \text{ g}$$

$$\% \text{ of } \text{CaCO}_3 = \frac{2.4375 \times 100}{3.75} = 65\%$$

$$\% \text{ of } \text{MgCO}_3 = 100 - 65 = 35\%$$

b. $\text{HCl used} = 2 \times \text{mol of } \text{CO}_2 = 2 \times 0.04 = 0.08 \text{ mol}$

c. $\text{HCl left} = \text{Mol of HCl added} - \text{Mol of HCl used}$
 $= 1 \text{ L} \times 0.1 - 0.08 = 0.02 \text{ mol}$

CONCEPT APPLICATION EXERCISE 3.4

Subjective Type

- 0.5 g of a mixture of K_2CO_3 and Li_2CO_3 requires 15 mL of 0.25 N HCl for neutralisation. Calculate the percentage composition of the mixture.
- Find the molality of 1.0 L solution of 90% H_2SO_4 by weight/volume. The density of the solution is 1.47 g cc^{-1} .
- What volume of 0.25 M H_2SO_4 is required to neutralise 1.90 g of a mixture containing equimolar amounts of NaHCO_3 and Na_2CO_3 ?
 (molar mass of NaHCO_3 is 84, Na_2CO_3 is 106)

ANSWERS

Subjective Type

1. 96.0%, 4% 2. 16.11 m 3. 60 mL

ILLUSTRATION 3.48

1.5 g of chalk was treated with 10 mL of 4N HCl. The chalk was dissolved and the solution was made to 100 mL. 25 mL of this solution required 18.75 mL of 0.2N NaOH solution for complete neutralisation. Calculate the percentage of pure CaCO_3 in the sample of chalk.

Sol. Excess of HCl in 25 mL = $18.75 \times 0.2 \text{ mEq}$

$$\text{Excess of HCl in 100 mL} = 18.75 \times 0.2 \times 4 = 15 \text{ mEq}$$

$$\text{Total HCl used} = 10 \times 4 = 40 \text{ mEq}$$

$$\text{HCl used} = 40 - 15 = 25 \text{ mEq} = 25 \text{ mEq of } \text{CaCO}_3$$

$$= 25 \times 10^{-3} \times 50 \text{ g of } \text{CaCO}_3 = 1.25 \text{ g}$$

$$\% \text{ of } \text{CaCO}_3 = \frac{1.25 \times 100}{1.5} = 83.33\%$$

ILLUSTRATION 3.49

10 g of a mixture of Cu_2S and CuS was titrated with 200 mL of 0.75 M MnO_4^- in acidic medium producing SO_2 , Cu^{2+} , and Mn^{2+} . The SO_2 was boiled off and the excess of MnO_4^- was titrated with 175 mL of 1 M Fe^{2+} solution. Find the percentage of CuS in the original mixture.

Sol. Total $\text{MnO}_4^- = 200 \times 0.75 \text{ M MnO}_4^-$
 $= 150 \times 5 \text{ mEq of MnO}_4^-$
 $= 750 \text{ mEq of MnO}_4^-$

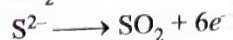
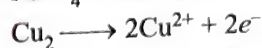
$$\text{Excess of MnO}_4^- = 175 \text{ mL of M Fe}^{2+}$$

$$= 175 \text{ m mol of Fe}^{2+}$$

$$= 175 \text{ mEq of Fe}^{2+}$$

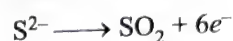
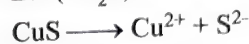
$$= 175 \text{ mEq of MnO}_4^-$$

$$\text{MnO}_4^- \text{ used up} = 750 - 175 = 575 \text{ mEq}$$



1 mol of Cu_2S requires $8e^-$

$$E_w (\text{Cu}_2\text{S}) = 159/8$$



1 mol of CuS requires $6e^-$

$$\therefore \text{Equivalent weight of CuS} = 95.5/6$$

$$\therefore x \text{ g of } \text{Cu}_2\text{S} \text{ and } (10 - x) \text{ g of CuS react.}$$

$$\therefore \left(\frac{x}{159/8} + \frac{10 - x}{95.5/6} \right) \times 1000 = 575$$

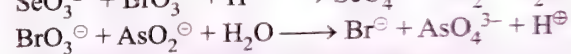
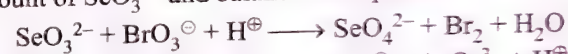
$$\therefore x = \text{Weight of } \text{Cu}_2\text{S} = 4.25 \text{ g}$$

$$\therefore \text{Weight of CuS} = 5.75 \text{ g}$$

$$\% \text{ of CuS} = 57.5\%$$

ILLUSTRATION 3.50

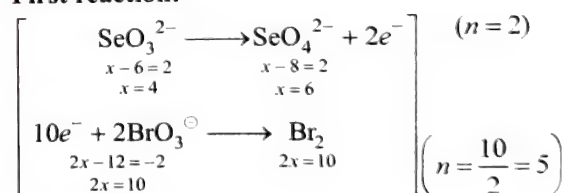
20 mL of M/60 KBrO_3 was added to a sample of SeO_3^{2-} . The bromine evolved was removed and the excess of KBrO_3 was titrated with 5.1 mL of M/25 solution of NaAsO_2 . Calculate the amount of SeO_3^{2-} and balance the equations.



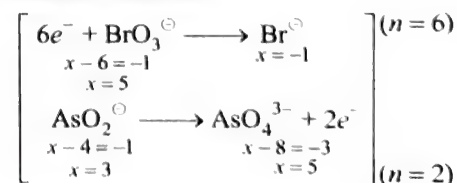
$$(\text{Br} = 80, \text{K} = 39, \text{As} = 75, \text{Se} = 79)$$

Sol. This question cannot be solved by the equivalent method, since the numbers of electrons in the two reactions are different. The n -factors for BrO_3^- to Br_2 and BrO_3^- to Br^- are different. So it has to be solved by mol method by balancing the two equations.

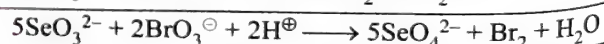
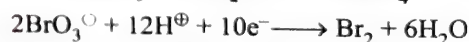
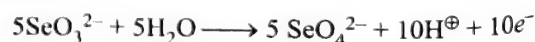
First reaction:

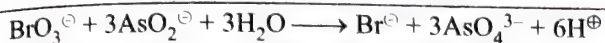
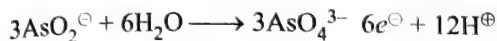
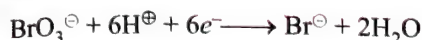


Second reaction:



First reaction:



Second reaction:

$$\text{Excess of KBrO}_3 = 5.1 \times \frac{1}{25} = 0.204 \text{ m mol}$$

$$= 0.204 \text{ mmol of NaAsO}_2$$

$$\therefore 3 \text{ mmol of AsO}_2^- = 1 \text{ mmol of KBrO}_3$$

$$0.204 \text{ mmol of AsO}_2^- = 0.068 \text{ m mol of KBrO}_3$$

$$\text{Total KBrO}_3 = 20 \times \frac{1}{60} = 0.333 \text{ mmol}$$

$$\text{KBrO}_3 \text{ used} = 0.333 - 0.068 = 0.265 \text{ mmol}$$

$$2 \text{ mmol of BrO}_3^- = 5 \text{ mol of SeO}_3^{2-}$$

$$0.265 \text{ mmol of BrO}_3^- = \frac{5}{2} \times 0.265 = 0.6625 \text{ mmol of SeO}_3^{2-}$$

$$(\text{Molecular weight of SeO}_3^{2-} \text{ is } 127)$$

$$\Rightarrow 0.6625 \times 10^{-3} \times 127 \text{ g of SeO}_3^{2-}$$

$$= 0.8143 \text{ g of SeO}_3^{2-}$$

ILLUSTRATION 3.51

30 mL of a solution containing 9.15 g L⁻¹ of an oxalate K_xH_y(C₂O₄)_z·nH₂O required for titration 27 mL of 0.12 N NaOH and 36 mL of 0.12 N KMnO₄ for oxidation. Find x, y, z, and n.

Sol. K_xH_y(C₂O₄)_z·nH₂O

$$\text{Normality of oxalate as an acid} = \frac{27 \times 0.12}{30} = 0.108$$

Ew of oxalate as acid

$$= \frac{\text{Strength}}{\text{N}} = \frac{9.15}{0.108} = 84.72$$

$$\text{Normality of oxalate as reducing agent} = \frac{36 \times 0.12}{30} = 0.144$$

$$\text{Ew of oxalate as reducing agent} = \frac{9.15}{0.144} = 63.54$$

$$\text{Oxalate as acid: } \frac{Mw}{y} = 84.72$$

$$\text{Oxalate as reducing agent } \frac{Mw}{2z} = 63.54$$

$$x + y = 2z$$

$$y = 1.5z$$

$$\therefore x:y:z = 1:3:2$$

$$\therefore 39 \times 1 + 3 \times 1 + 2 \times 88 + 18n = 254$$

$$n = 2$$

$$\text{Formula is K} \text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}.$$

ILLUSTRATION 3.52

The neutralisation of a 1.20 g solution of a mixture of H₂C₂O₄·2H₂O and KHC₂O₄·H₂O and different impurities of a neutral salt consumed 37.80 mL of 0.25 N NaOH solution. On the other hand, on titration with KMnO₄ for 0.40 g of the same substance, 43.10 mL of 0.125 N KMnO₄ was required. Find the percentage composition of the substance being analysed.

Sol. Let the percentage of H₂C₂O₄·2H₂O be *a*% and the percentage of KHC₂O₄·H₂O be *b*%.

a. H₂C₂O₄·2H₂O as an acid has 2H⁺ ions.

$$\therefore \text{'n' factor} = 2,$$

$$Mw = 126, Ew = 126/2 = 63 \text{ g mol}^{-1}$$

KHC₂O₄·H₂O as an acid has H⁺ ion.

$$\therefore \text{'n' factor} = 2.$$

$$Mw = Ew = 146.$$

$$\frac{1.2}{100} \left(\frac{a}{63} + \frac{b}{146} \right) \times 1000 = 37.80 \times 25$$

b. Both H₂C₂O₄·2H₂O and KHC₂O₄·H₂O, when act as reducing agents, C₂O₄²⁻ changes to 2CO₂, therefore in both cases 'n' factor = 2.

$$Ew \text{ of H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 63 \text{ g mol}^{-1}$$

$$Ew \text{ of KHC}_2\text{O}_4 \cdot \text{H}_2\text{O} = \frac{146}{2} = 73 \text{ g mol}^{-1}$$

$$\frac{0.40}{100} \left(\frac{a}{63} + \frac{b}{73} \right) \times 1000 = 43.10 \times 0.125$$

$$\therefore a = \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 14.3\%$$

$$b = \text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O} = 81.7\%$$

ILLUSTRATION 3.53

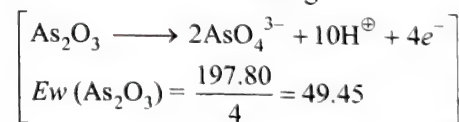
A sample of pyrolusite (MnO₂) weighs 0.5 g. To its solution, 0.6674 g of As₂O₃ and dilute acid are added. After the reaction has ceased, Arsenic (As³⁺) in As₂O₃ is titrated with 45 mL of M/50 KMnO₄ solution. Calculate the percentage of MnO₂ in pyrolusite. (Atomic weight of As is 74.9 and that of Mn is 55.)

Sol. mEq of KMnO₄ = $45 \times \frac{1}{10} = 4.5$

$$\text{Unreacted As}_2\text{O}_3 = 4.5 \text{ mEq}$$

$$= 4.5 \times 10^{-3} \times 49.5 \text{ g of As}_2\text{O}_3$$

$$= 0.222 \text{ g}$$



$$\text{Amount of As}_2\text{O}_3 \text{ reacted} = 0.6674 - 0.222$$

$$= 0.4448 \text{ g}$$

$$= \frac{0.4448}{49.45} = 0.0089 \text{ Eq of As}_2\text{O}_3$$

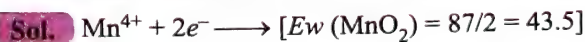
$$[Ew(\text{MnO}_2) = 87/2 = 43.5]$$

$$= 0.0089 \times 43.5 \text{ g of MnO}_2 = 0.39 \text{ g of MnO}_2$$

$$\% \text{ of MnO}_2 = \frac{0.39}{0.5} \times 100 = 78.2\%$$

ILLUSTRATION 3.54

0.6 g of a sample of pyrolusite was boiled with 200 mL of N/10 oxalic acid and excess of dilute sulphuric acid. the liquid was filtered and the residue washed. The filtrate and washing were mixed and made up to 500 mL in a measuring flask. 100 mL of this solution required 50 mL of N/30 KMnO₄ solution. Calculate the percentage of MnO₂ in the sample (Mn = 55).



$$\text{Total oxalic acid used} = 200 \times \frac{1}{10} = 20 \text{ mEq}$$

Excess of oxalic acid

$$= 50 \times 1/30$$

$$= \frac{5}{3} \text{ mEq, of KMnO}_4 \text{ in 100 mL}$$

$$= \frac{5}{3} \times 5 = \frac{25}{3} \text{ mEq, of KMnO}_4 \text{ in 500 mL}$$

$$= \frac{25}{3} \text{ mEq, of oxalic acid in 500 mL}$$

$$\text{Oxalic acid used} = 20 - \frac{25}{3} = \frac{35}{3} \text{ mEq}$$

$$= \frac{35}{3} \text{ mEq of MnO}_2$$

$$= \frac{35}{3} \times 10^{-3} \times 43.5 \text{ g of MnO}_2$$

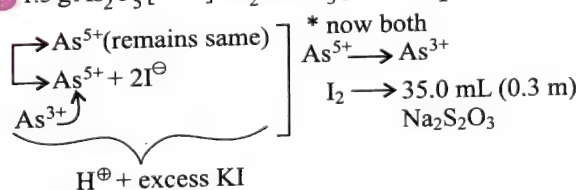
$$= 0.5075 \text{ g of MnO}_2$$

$$\% \text{ of MnO}_2 = \frac{0.5075 \times 100}{0.6} = 84.583\%$$

ILLUSTRATION 3.55

1.5 g of a mixture containing As_2O_5 , Na_2HASO_3 , and some inert impurities is dissolved in water, and the solution is kept neutral by adding excess of NaHCO_3 . The solution when titrated with 0.1 M I_2 required 35.0 mL of it for complete titration. The solution is then acidified and excess of KI is added to it. The I_2 liberated required 35.0 mL of 0.3 M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete titration. Find the percentage composition of the mixture (Atomic mass of As is 75, Na is 23, and O is 16).

Sol. 1.5 g As_2O_5 [As^{5+}] Na_2HASO_3 [As^{3+}] + I_2 (35.0 mL of 0.1 M)



In first experiment

$$\text{mEq of Na}_2\text{HASO}_3 = \text{mEq of I}_2$$

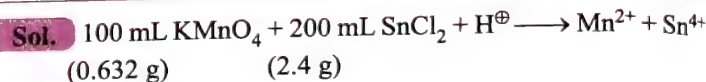
$$\frac{g}{E} \times 1000 = 2 \times 0.1 \times 35$$

$$g = \frac{2 \times 0.1 \times 35 \times E}{1000} \quad \left(E = \frac{170}{2} \right)$$

$$= 0.595 \text{ g } \% \text{ Na}_2\text{HASO}_3 = 39.67\%$$

ILLUSTRATION 3.56

To 100 mL of KMnO_4 solution containing 0.632 g of KMnO_4 , 200 mL of SnCl_2 containing 2.4 g is added in presence of HCl. To the resulting solution, an excess of HgCl_2 is added at once. How many grams of Hg_2Cl_2 will be precipitated? (molecular mass of KMnO_4 is 158, SnCl_2 is 95, and Hg_2Cl_2 is 471 g mol^{-1})



$$\text{mEq of KMnO}_4 = \frac{0.632 \times 1000}{158/5} = 20$$

$$\text{mEq of SnCl}_2 = \frac{2.4}{190/2} \times 1000 = 25.26$$

$\Rightarrow \text{SnCl}_2$ is in excess

$$\text{Excess mEq of SnCl}_2 = 5.26$$

$$\text{mmol of SnCl}_2 = \frac{1}{2} \times 5.26 = 2.63$$



$$\Rightarrow 1 \text{ mol SnCl}_2 \equiv 1 \text{ mol Hg}_2\text{Cl}_2$$

$$\begin{aligned} \Rightarrow \text{mol Hg}_2\text{Cl}_2 \text{ formed} &= 2.6 \times 10^{-3} \\ &\equiv 2.6 \times 10^{-3} \times 471 \text{ g} \\ &= 1.225 \text{ g} \end{aligned}$$

ILLUSTRATION 3.57

3.0 g of impure Na_2CO_3 is dissolved in water and the solution is made up to 250 mL. To 50 mL of this solution, 50 mL of 0.1 N HCl is added and the mixture, after shaking well, required 10 mL of 0.16 N NaOH solution for complete neutralisation. Calculate the percentage purity of the sample of Na_2CO_3 .

Sol. Excess mEq of HCl = mEq of NaOH
 $= 0.16 \times 10 = 1.6$

$$\text{mEq of HCl added} = 0.1 \times 50 = 5.0$$

$$\Rightarrow \text{mEq of HCl used against Na}_2\text{CO}_3 = 5.0 - 1.6 = 3.4$$

$$\text{Also mEq of Na}_2\text{CO}_3 = 5.0 - 1.6 = 3.4 \text{ (in 50 mL)}$$

$$\equiv 17 \text{ (in 250 mL)}$$

$$\Rightarrow \frac{g}{106/2} \times 1000 = 17 \Rightarrow g = 0.901$$

$$\% \text{ purity} = \frac{0.901}{3} \times 100 = 30.03$$

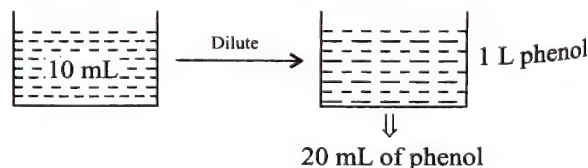
ILLUSTRATION 3.58

10 mL of a sample of phenol was diluted with H_2O and made up to 1.0 L. 20 mL of this solution was treated with 40 mL brominating solution (a mixture of KBrO_3 and KBr) in dil H_2SO_4 . Excess of KI was added, and the liberated I_2 required 15 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ for complete reaction. 25 mL of the same brominating solution, on similar treatment required, 20 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$. Calculate the weight of phenol per litre of the original sample.

(Brominating mixture:



Sol.



Blank titration:

25 mL of brominating solution \equiv 20 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$
 $(2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + 2e^-)$

$$n = \frac{2}{2} = 1$$

(Molarity = Normality)

Normality of brominating mixture

$$N_1 V_1 (\text{brominating mixture}) = N_2 V_2 (\text{S}_2\text{O}_3^{2-})$$

$$N_1 \times 25 = 0.1 \times 1 \times 20$$

$$N_1 = \frac{0.1 \times 20}{25} = \frac{2}{25}$$

Titration of brominating mixture \equiv phenol

mEq of brominating mixture \equiv mEq of phenol

$$40 \text{ mL} \times \frac{2}{25} \text{ N} = \text{Total mEq}$$

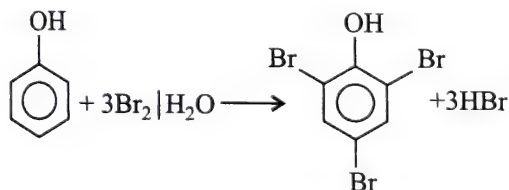
$$\begin{aligned} \text{Excess of brominating mixture} &= \text{mEq of } \text{S}_2\text{O}_3^{2-} \\ &= 15 \times 0.1 \times 1 = 15 \text{ mEq} \end{aligned}$$

Reacted brominating mixture with phenol

$$= 40 \times \frac{2}{25} - (15 \times 0.1) = 1.7 \text{ mEq}$$

mEq of $\text{Br}_2 = 1.7$

$$\text{m mol of } \text{Br}_2 = \frac{1.7}{2} \quad (\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-)$$



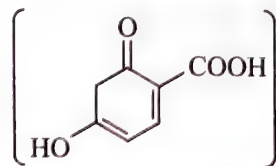
1 mol of phenol \equiv 3 mol of Br_2

$$\begin{aligned} \text{mmol of phenol} &= \frac{1}{3} \times \frac{1.7}{2} \\ &= \frac{1}{3} \times \frac{1.7}{2} \times 10^{-3} \times 94 \text{ g} / 20 \text{ mL} \\ &\equiv \frac{1.7}{6} \times 10^{-3} \times 94 \times 50 \text{ g} \times 10 \text{ mL of original solution} \\ &= \left[\frac{1.7}{6} \times 10^{-3} \times 94 \times 50 \right] \times 100 \text{ g L}^{-1} \\ &\equiv 133.16 \text{ g L}^{-1} \end{aligned}$$

$\therefore 133.16 \text{ g L}^{-1}$ of phenol.

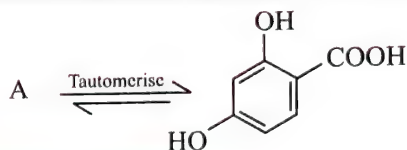
ILLUSTRATION 3.59

1 mol of an organic compound (A)

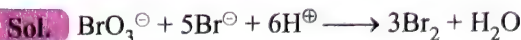


reacts with NaOH. How many moles of NaOH are required to react with (A)?

Sol. 3 mol, because it has three acidic H^+ ions.

**ILLUSTRATION 3.60**

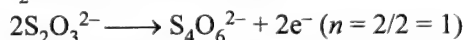
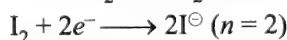
A sample of pure aniline was dissolved in HCl and diluted to 100 mL with H_2O . 20 mL of liquid was treated with 25 mL of 0.017 M KBrO_3 and about 10 g KBr was added to form Br_2 . After 10 min, an excess of KI was added, and the liberated I_2 was titrated with 12.92 mL of 0.12 M $\text{Na}_2\text{S}_2\text{O}_3$. Calculate the weight of aniline taken.



1 mol of $\text{BrO}_3^- \equiv$ 3 mol of Br_2

$$25 \times 0.017 \text{ mmol} = 3 \times 25 \times 0.017 \text{ mmol of } \text{Br}_2$$

Reactions involved are

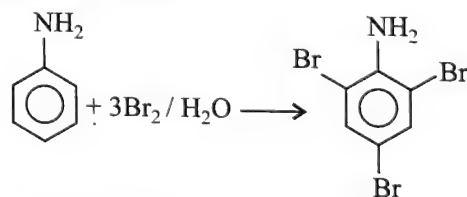


Excess of $\text{Br}_2 \equiv$ moles of I_2

$$\begin{aligned} \text{mEq of } \text{Na}_2\text{S}_2\text{O}_3 &= 12.92 \times 0.12 \times 1 \\ &= 12.92 \times 0.12 \text{ mEq of } \text{I}_2 \\ &= \frac{12.92 \times 0.12}{2} \text{ mmol of } \text{I}_2 \end{aligned}$$

$$\begin{aligned} \text{Br}_2 \text{ reacted with aniline} &= \left(3 \times 25 \times 0.017 - \frac{12.92 \times 0.12}{2} \right) \\ &= 12.75 - 0.7725 \\ &= 0.4998 \text{ mmol of } \text{Br}_2 \\ &\approx 0.5 \text{ mmol of } \text{Br}_2 \end{aligned}$$

[Mw (aniline) = 93]

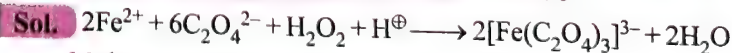


3 mmol of $\text{Br}_2 =$ 1 mmol of aniline

$$\begin{aligned} 0.5 \text{ mmol of } \text{Br}_2 &= \frac{1}{3} \times 0.5 \text{ mmol of aniline} \\ &= \frac{0.5}{3} \times 10^{-3} \times 93 = 0.0155 \text{ g} \end{aligned}$$

ILLUSTRATION 3.61

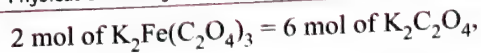
In the reaction of Mohr's salt $[\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ with oxalate ions in the presence of H_2O_2 and H^+ ions, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ion is formed. Calculate the minimum mass of Mohr's salt and $\text{K}_2\text{C}_2\text{O}_4$ required to prepare 10 g of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$.



Molecular weight of Mohr's salt = 392

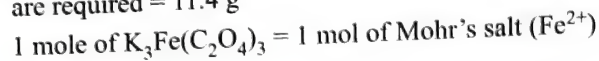
Molecular weight of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 = 437$

Molecular weight $\text{K}_2\text{C}_2\text{O}_4 = 166$



$$\frac{10}{437} \text{ mol of } K_3Fe(C_2O_4)_3 = \frac{6}{2} \times \frac{10}{437} \times 166 \text{ g of } K_2C_2O_4$$

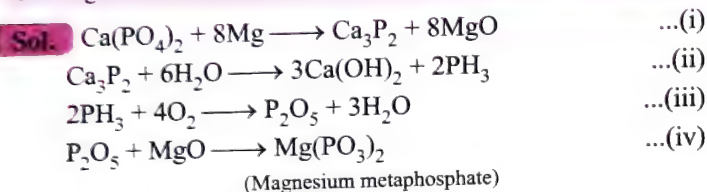
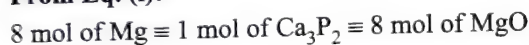
are required = 11.4 g



$$\frac{10}{437} \text{ mol of } K_3Fe(C_2O_4)_3 = \frac{10}{437} \times 392 = 8.97 \text{ g}$$

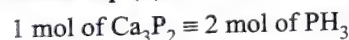
ILLUSTRATION 3.62

Calcium phosphide formed by reacting calcium orthophosphate with Mg was hydrolysed by water. The phosphine evolved was burnt in air to yield P_2O_5 . How many litres of air, containing 21% by volume of O_2 , was required to burn PH_3 and how many grams of magnesium metaphosphate would be obtained if 204 g of Mg was used for reducing calcium phosphide and the volumes of the gases were measured at STP?

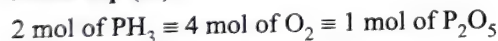
**From Eq. (i):**

$$\frac{2.4}{24} = 0.1 \text{ mol of Mg} \equiv \frac{0.1}{8} \text{ mol of } Ca_3P_2$$

$$\equiv 0.1 \text{ mol of MgO}$$

From Eq. (ii):

$$\frac{0.1}{8} \text{ mol of } Ca_3P_2 \equiv \frac{0.1}{4} \text{ mol of } PH_3$$

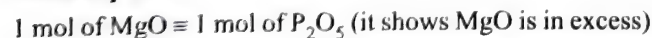
From Eq. (iii):

$$\frac{0.1}{4} \text{ mol of } PH_3 \equiv \frac{4}{2} \times \frac{0.1}{4} \text{ mol of } O_2$$

$$\equiv \frac{1}{2} \left(\frac{0.1}{4} \right) \text{ mol of } P_2O_5$$

$$\equiv 0.05 \times 22.4 \text{ L of } O_2 \text{ at STP} \equiv 1.12 \text{ L}$$

$$\equiv \frac{100}{21} \times 1.12 \text{ L of air} \equiv 5.33 \text{ L of air}$$

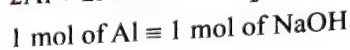
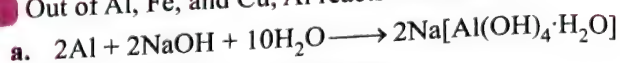
From Eq. (iv)

$$0.1 \text{ mol of MgO} \equiv \frac{0.1}{8} \text{ mol}$$

$$\text{Weight of metaphosphate formed} \equiv \frac{0.1}{8} \times 182 = 2.275 \text{ g}$$

ILLUSTRATION 3.63

A mixture of Cu, Fe, and Al was reacted with 13.33 g of NaOH. During chlorination with the same amount of metal mixture entered into reaction with 12.5 L of chlorine measured at STP, while for treating the same amount of the metal mixture 343.64 mL of HCl, having a density of 1.1 g mL^{-1} and containing 10% by mass of HCl were required. Determine the mass percentage of the metals in the mixture.

Sol. Out of Al, Fe, and Cu, Al reacts with NaOH.

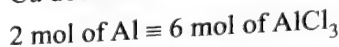
$$\equiv \left(\frac{13.33}{40} \right) \text{ mol of NaOH}$$

$$\equiv \left(\frac{13.33}{40} \right) \text{ mol of Al}$$

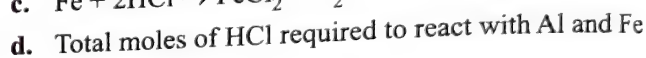
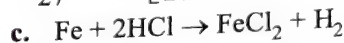
$$\equiv \frac{13.33}{40} \times 27 \text{ g of Al} = 9 \text{ g of Al}$$



Cu does not react with HCl.



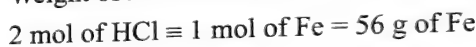
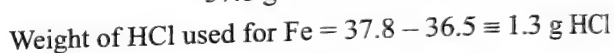
$$\frac{9}{27} \text{ mol} = \left[\frac{9}{27} \times 3 \right] \times 36.5 \equiv 36.5 \text{ g of HCl is used for Al}$$



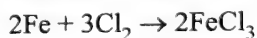
$$= M \times V_L$$

$$\text{Weight of HCl} = \left(\frac{10 \times 10 \times 1.1}{36.5} \times \frac{343.64}{1000} \right) \times 36.5$$

$$= 37.8 \text{ g}$$



$$\left(\frac{1.3}{36.5} \right) \text{ mol of HCl} \equiv \left(\frac{56}{2} \times \frac{1.3}{36.5} \right) \equiv 0.997 \text{ g Fe}$$

All these metals react with Cl_2 

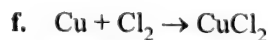
$$\text{Volume of } Cl_2 \text{ at STP} = \left(\frac{3}{2} \times \frac{0.997}{56} \right) \times 22.4 \text{ L}$$

$$= 0.598 \text{ L at STP}$$



$$\text{Volume of } Cl_2 \text{ at STP} = \left(\frac{3}{2} \times \frac{9}{27} \right) \times 22.4$$

$$= 11.2 \text{ L of } Cl_2$$



$$\text{Volume of } Cl_2 \text{ at STP} = (12.5 - 11.2 - 0.598)$$

$$= 0.702 \text{ L of } Cl_2$$

$$\text{Weight of Cu} = \frac{0.7}{22.4} \times 63.5 = 1.99 \text{ g Cu}$$

$$Al = 9 \text{ g, Fe} = 0.997 \text{ g, Cu} = 1.99 \text{ g}$$

$$\text{Total weight} = 11.987 \text{ g}$$

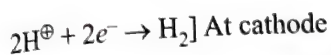
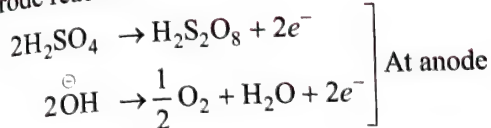
$$\% Al = 75.08, \quad \% Fe = 8.31, \quad \% Cu = 16.6$$

ILLUSTRATION 3.64

Perdisulphuric acid ($H_2S_2O_8$) or Marshall's acid can be prepared by the electrolytic oxidation of H_2SO_4 . At anode O_2 and H_2 are obtained as side products. After passing a current of 0.5 A for a certain time, the volume of H_2 and O_2 collected was found to be 10.08 and 2.24 L, respectively, at STP. What is the weight of $H_2S_2O_8$ produced during the same time? Also find the duration of electrolysis (in seconds) assuming 75% efficiency of electrolysis. Give all the electrode reactions.

Sol.

a. Electrode reactions:



Since two reactions are occurring at anode and one reaction at cathode, number of equivalent of $\text{H}_2\text{S}_2\text{O}_8$ + number of equivalent of O_2 = number of equivalent of H_2 .

Let the weight of $\text{H}_2\text{S}_2\text{O}_8$ be x g

$$\text{Eq of } \text{H}_2\text{S}_2\text{O}_8 = \frac{x}{194/2}$$

$$1 \text{ mol of } \text{H}_2 = 2 \text{ Eq of } \text{H}_2 = 22.4 \text{ L at STP}$$

$$\text{Eq of } \text{H}_2 = \frac{10.08}{22.4/2}$$

$$1 \text{ mol of } \text{O}_2 = 4 \text{ Eq of } \text{O}_2 = 22.4 \text{ L}$$

$$\text{Eq of } \text{O}_2 = \frac{2.24}{22.4/4}$$

$$\therefore \text{Eq of } \text{H}_2\text{S}_2\text{O}_8 + \text{Eq of } \text{O}_2 = \text{Eq of } \text{H}_2$$

$$\frac{x}{194/2} + \frac{2.24}{22.4/4} = \frac{10.08}{22.4/2}$$

$$\frac{x}{97} + 0.4 = 0.9 \therefore x = 48.5 \text{ g}$$

$$\text{Weight of } \text{H}_2\text{S}_2\text{O}_8 = 48.5 \text{ g}$$

b. At cathode, only one reaction takes place, so the number of faradays for electrolysis can be calculated from cathode reaction.

$$1 \text{ Eq of } \text{H}_2 \text{ gas} = 1 \text{ F}$$

$$\therefore \frac{10.08}{11.2} \text{ Eq} = 0.9 \text{ F}$$

For 75% efficiency,

$$\text{Number of faradays delivered} = 0.9 \times \frac{100}{75}$$

$$= \frac{90}{75} \times 96500 \text{ Coulomb}$$

$$I \times t = \frac{90 \times 96500}{75}$$

$$5 \times t = \frac{90 \times 96500}{75}$$

$$t = 23160 \text{ s} = 6.43 \text{ hr}$$

Sol.

mEq of excess of oxalic acid

$$= 32 \times 0.1 \text{ in } 25 \text{ mL}$$

$$= 32 \times 0.1 \times \frac{250}{25} \text{ in } 250 \text{ mL}$$

$$= 32 \text{ mEq}$$

$$\text{Total oxalic acid used} = 50 \times 1 = 50 \text{ mEq}$$

$$\text{mEq of oxalic acid used for } \text{MnO}_2 = 50 - 32 = 18$$

$$\text{mEq of } \text{MnO}_2 = 18$$

$$= 18 \times 10^{-3} \times \frac{87}{2} \text{ g of } \text{MnO}_2$$

$$= 0.783 \text{ g}$$

$$\% \text{ of } \text{MnO}_2 = \frac{0.783}{1.6} \times 100 = 48.93\%$$

$$\text{mEq of } \text{MnO}_2 = \text{mEq of } \text{O}_2$$

$$\therefore \text{mEq of } \text{O}_2 = 18$$

$$\text{Weight of } \text{O}_2 = 18 \times 10^{-3} \times 8 = 0.144 \text{ g (1 Eq of } \text{O}_2 = 8 \text{ g)}$$

$$\% \text{ of } \text{O}_2 = \frac{0.144}{1.6} \times 100 = 9\%$$

ILLUSTRATION 3.66

1.0 g NaHSO_3 and Na_2SO_3 was dissolved in water to prepare a 200 mL solution. Two separate experiments were carried out.

a. 25 mL of sample was mixed with 25 mL of I_2 solution and excess of I_2 left after the reaction with NaHSO_3 and Na_2SO_3 was back titrated with 0.1002 N $\text{Na}_2\text{S}_2\text{O}_3$, 1.34 mL of which was required (25 mL of I_2 solution is equivalent to 24.20 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution).

b. 50 mL of sample was oxidised to Na_2SO_4 by the action of H_2O_2 ; H_2SO_4 formed (from NaHSO_3) was titrated with 22.3 mL of 0.1 N NaOH. Find percentage of NaHSO_3 and Na_2SO_3 in the original sample.

Sol. 1 g mixture is present in 200 mL

a. 25 mL of mixture]

$$\Rightarrow \text{mEq of } \text{NaHSO}_3 + \text{mEq of } \text{Na}_2\text{SO}_3 = \text{mEq of } \text{I}_2 \text{ used}$$

$$\text{mEq of } \text{I}_2 \text{ used} = 24.20 - 1.34 \times 0.1002/25 \text{ mL}$$

$$= 22.905$$

$$\text{mEq of } \text{I}_2 \text{ in } 200 \text{ mL} = \frac{200}{25} \times 22.905 = 18.32$$

b. 50 mL is oxidised to Na_2SO_4

$$\text{H}_2\text{SO}_4 \text{ formed by } \text{NaHSO}_3 \equiv 22.3 \text{ mL of } 0.1 \text{ N NaOH}$$

$$\therefore \text{mEq of } \text{NaHSO}_3 = 22.3 \times 0.1 = 2.23/25 \text{ mL}$$

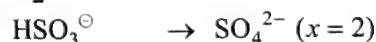
$$\text{mEq of } \text{NaHSO}_3 \text{ in } 200 \text{ mL} = 2.23 \times \frac{200}{50} = 8.92$$

ILLUSTRATION 3.65

1.6 g of pyrolusite ore was treated with 50 mL of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution, when titrated with 0.1 N KMnO_4 required 32 mL of this solution. Find out the percentage of pure MnO_2 and also the percentage of available oxygen from MnO_2 .

[Ew of NaHSO_3 in experiment

$$(i) = \frac{Mw}{2}$$



$$1 + x - 6 = -1$$

$$x - 8 = -2$$

$$x = 4$$

$$x = 6$$

$$\left[\begin{array}{l} \text{Eq of NaHSO}_3 \text{ in experiment} \\ \text{(ii)} = \frac{M_w}{1} \\ \text{HSO}_3^- \longrightarrow \text{H}^+ + \text{SO}_3^{2-} \end{array} \right]$$

$$\text{mEq of Na}_2\text{SO}_3 \text{ in the original solution} = 18.32 - 2 \times 8.92 = 0.48$$

$$\text{Weight of NaHSO}_3 = 8.92 \text{ mEq} \times \frac{1}{1000} \times \text{Eq of NaHSO}_3$$

$$\left[\begin{array}{l} \text{Eq of NaHSO}_3 = \frac{M_w}{1} = 104 \\ = \frac{8.92}{1000} \times 104 = 0.92 \end{array} \right]$$

$$\therefore \% \text{ of NaHSO}_3 = \frac{0.927}{1} \times 100 = 92.7 \%$$

$$\left[\begin{array}{l} \text{Equivalent weight of Na}_2\text{SO}_3 = \frac{M_w}{2} = \frac{126}{2} = 63 \end{array} \right]$$

$$\text{Weight of Na}_2\text{SO}_3 = 0.48 \text{ mEq} \times \frac{1}{1000} \times 63 = 0.3 \text{ g}$$

$$\% \text{ of Na}_2\text{SO}_3 = \frac{0.3}{1} \times 100 = 3\%$$

$$\text{NaHSO}_3 = 92.7\%, \quad \text{Na}_2\text{SO}_3 = 3\%$$

CONCEPT APPLICATION EXERCISE 3.5

Subjective Type

1. A solution of KMnO_4 containing 3 g L^{-1} , is used to titrate H_2O_2 solution containing 2 g L^{-1} . What volume of KMnO_4 will be required to react with 20 mL of H_2O_2 ? Also find strength of H_2O_2 solution in terms of available oxygen.
2. Two acids A and B are titrated separately each time with 25 mL of $\text{N-Na}_2\text{CO}_3$ solution to require 10 mL and 40 mL respectively, of their solution for complete neutralisation. What volume of A and B would you mix to produce 1 L of N-acid solution?
3. 1.00 g of a mixture, consisting of equal number of moles of carbonates of two alkali metals, required 44.4 mL of 0.5 N-HCl for complete reaction. If the atomic weight of one of the metal is 7.00 . Find the atomic weight of the other metal. What will be the total amount of sulphate formed on quantitative conversion of 1.00 g of the mixture into sulphates?
4. A sample of chalk (CaCO_3) is contaminated with calcium sulphate. 1.0 g of the solid is dissolved in 230 mL of N/10 HCl ; 40.1 N/10 NaOH is required to neutralise the excess acid. What is the percentage of chalk in the mixture.
5. The amount of CO in a gas sample can be determined by using the reaction

$$\text{I}_2\text{O}_5 + 5\text{CO} \longrightarrow \text{I}_2 + 5\text{CO}_2$$
 If a gas sample liberated 0.2 g of I_2 , how many g of CO were present in the sample.
6. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution.

The solution was acidified with HCl . The liberated I_2 consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

ANSWERS

Subjective Type

1. 0.66 V
2. $200 \text{ mL}, 800 \text{ mL}$
3. $1.4 \text{ g, at. wt.} = 23.09$
4. 95%
5. 0.110 g
6. $0.0623 \text{ mol L}^{-1}$

3.8 USE OF INDICATORS

- Acid-base titration:** The determination of the concentration of bases by titration with a standard acid is called *acidimetry* and the determination of the concentration of acids by titration with a standard base is called *alkalimetry*.
- Acid-base indicators:** The substances that give different colours with acids and bases are called *acid-base indicators*. These indicators are used in the visual detection of the equivalence point in acid-base titrations. They are also called pH indicators because their colour changes according to the pH of the solution.

Table 3.1 pH range of indicators

S. No.	Indicators	pH range	Colour of indicator	
			Acidic medium	Basic medium
1.	Methyl orange	3.1–4.5	Red	Orange
2.	Bromophenol blue	3.0–4.6	Yellow	Blue
3.	Methyl red	4.2–6.3	Red	Yellow
4.	Litmus	4.6–8.3	Red	Blue
5.	Bromothymol blue	6.0–7.6	Yellow	Blue
6.	Phenol red	6.8–8.4	Yellow	Red
7.	Phenolphthalein	8.0–9.8	Colourless	Pink
8.	Thymol blue	8.6–9.6	Yellow	Purple
9.	Thymolphthalein	8.3–10.5	Colourless	Blue

3.8.1 Selection of Indicators

In the selection of indicators for a titration, two points are taken into consideration:

- a. pH range of indicator
- b. pH range near the equivalence point in the titration.

The indicator whose pH range is included in the pH change of the solution near the equivalence point is taken as a suitable indicator for the titration.

Strong Acid–Strong Base Titration

In the titration of HCl with NaOH , the equivalence point lies in the pH range of 3.0 – 10.5 . Thus, any indicator whose pH range lies in that range would be suitable, but the most ideal would be that which shows colour changes very near to the end point ($\text{pH} = 7$).

Thus bromothymol blue having pH range 6.0–7.6 is most suitable. Phenolphthalein (8.0–9.8) and methyl orange (3.1–4.5) are most suitable indicators.

Phenolphthalein is, however, most suitable when an alkali is used as titrant, while methyl orange is most suitable when an acid is used as titrant.

Weak Acid–Strong Base Titration

In the titration of CH_3COOH and NaOH , pH range at the end point is 8–10. Since the pH range near the end point lies on the alkaline side, phenolphthalein and thymol blue are suitable indicators.

Weak Base–Strong Acid Titration

In the titration of NH_4OH and HCl , pH at the end point is 3.0–6.0. Thus, methyl orange, methyl red, and bromophenol blue are suitable indicators.

Weak Acid–Weak Base Titration

In the titration of CH_3COOH and NH_4OH satisfactorily there is no sharp change at the end point and pH varies between 6.0 and 8.0. Thus, no indicator can function satisfactorily in such titration. Approximate end point is possible with phenol red (pH range 6.8–8.4).

ILLUSTRATION 3.67

There are three acid-base indicators. Methyl orange (end point at pH = 4), bromothymol blue (end point at pH = 7), phenolphthalein (end point at pH = 9). Which is the most suitable indicator for the following titrations?

- | | |
|--|-----------------------------------|
| a. H_2SO_4 with KOH | b. KCN with HCl |
| c. NH_3 with HNO_3 | d. HF with NaOH |

Sol.

- Strong acid and strong base: Any indicator can be used.
- Strong acid and salt of weak acid and strong base: Methyl orange is suitable.
- Weak base and strong acid: Methyl orange
- Strong base and weak acid: Phenolphthalein

3.8.2 Use of Double Indicators in Neutralisation

In the titration of a mixture of NaOH and Na_2CO_3 ; NaOH and NaHCO_3 , Na_2CO_3 and NaHCO_3 ; and NaOH , NaHCO_3 ; and Na_2CO_3 , two indicators *phenolphthalein* and *methyl orange* are used.

- Phenolphthalein (weak organic acid):** It gives colour change in the pH range of 8–10.
 - It indicates complete neutralisation of NaOH or KOH (strong base).
 - It indicates half neutralisation of Na_2CO_3 and at the end point, NaHCO_3 is formed.
 - It fails to indicate the neutralisation of NaHCO_3 at all because CO_2 is the product of the final neutralisation of NaHCO_3 .

CO_2 is an acidic oxide and in acidic medium, phenolphthalein does not respond.

- Methyl orange (weak organic base):** It gives colour change in the pH range of 3.0–4.4. Due to lower pH range, it indicates complete neutralisation of whole of the base, i.e., at the end point (colour change for indicator) the above mixtures are fully neutralised. So in the analysis of such alkali mixtures, both the indicators are used one after the other in the same volumetric mixture successively or two indicators are used independently in two different titrations.

For example:

- In the neutralisation mixture of NaOH and Na_2CO_3

- Use of methyl orange:** NaOH and Na_2CO_3 both are neutralised completely, i.e.,

$$\text{mEq of NaOH} + \text{mEq of Na}_2\text{CO}_3 = \text{mEq of acid used.}$$

Volume of acid for complete neutralisation of

$$\text{NaOH} + \text{Na}_2\text{CO}_3 = \text{Volume of acid at the end point}$$

- Use of phenolphthalein:** NaOH is fully neutralised and Na_2CO_3 is half neutralised, i.e.,

$$\text{mEq of NaOH} + \frac{1}{2}(\text{mEq of Na}_2\text{CO}_3)$$

$$= \text{mEq of acid used}$$

or volume of acid for complete neutralisation of NaOH

$$+ \frac{1}{2} \text{ volume of acid for complete neutralisation of}$$

$$\text{Na}_2\text{CO}_3 = \text{volume of acid at the end point}$$

- In the neutralisation of NaHCO_3 and Na_2CO_3

- Use of methyl orange:** NaHCO_3 and Na_2CO_3 both are fully neutralised, i.e.,

$$\text{mEq of NaHCO}_3 + \text{mEq of Na}_2\text{CO}_3 = \text{mEq of acid used.}$$

or

$$\text{Volume of acid for complete neutralisation of NaHCO}_3 + \text{Na}_2\text{CO}_3 = \text{volume of acid at the end point}$$

- Use of phenolphthalein:** NaHCO_3 is *not* neutralised at all, but Na_2CO_3 is half neutralised, i.e.,

$$\frac{1}{2} \text{ mEq of Na}_2\text{CO}_3 = \text{mEq of acid used}$$

or

$$\frac{1}{2} (\text{Volume of acid for complete neutralisation of}$$

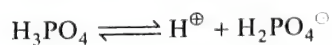
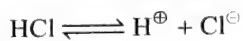
$$\text{Na}_2\text{CO}_3)$$

$$= \text{Volume of acid at the end point}$$

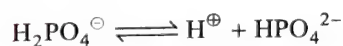
3.8.3 Summary of Indicators Used

- Indicator in acid–base titration
 - Strong acid versus strong base (methyl orange)
 - Strong acid versus weak base (methyl red)
 - Weak acid versus strong base (phenolphthalein)
- Methyl orange indicates 100% reaction of any type of base (NaOH , Na_2CO_3 , NaHCO_3) with acid.
- Phenolphthalein indicates 100% reaction of NaOH , 50% of Na_2CO_3 (up to NaHCO_3) and no reaction of NaHCO_3 .

- d. In the titration of mixture of HCl and H_3PO_4 by NaOH
 i. Methyl red indicates complete ionisation of HCl and first step ionisation of H_3PO_4



- ii. Bromothymol blue indicates second step ionisation of H_3PO_4 i.e.,



- iii. Methyl orange indicates first step ionisation of



Table 3.2 Result with two indicators

Mixture	Method I		Method II	
	Volume of HCl used with indicator		Volume of HCl used with indicator	
	Phenolphthalein	Methyl orange	Phenolphthalein	Methyl orange added after first end point is reached
1. $\text{NaOH} + \text{Na}_2\text{CO}_3$	$\left(z + \frac{x}{2}\right)$ ↑ 100% 50%	$(x + z)$ 100% each	$\left(z + \frac{x}{2}\right)$ ↑ 100% 50%	$\frac{x}{2}$ (remaining 50% Na_2CO_3 is indicated)
2. $\text{NaOH} + \text{NaHCO}_3$	z + 0 ↑ 100% No reaction	$(y + z)$ 100% each	$(z + 0)$	(remaining 100% NaHCO_3 is indicated)
3. $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$	$\frac{x}{2}$ + 0 ↑ 50% No reaction	$(x + y)$ 100% each	$\left(\frac{x}{2} + 0\right)$	$\left(\frac{x}{2} + y\right)$ (remaining 50% of Na_2CO_3 and 100% NaHCO_3 are indicated)

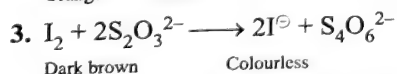
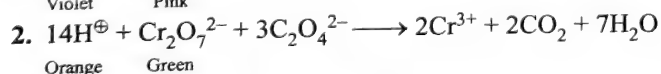
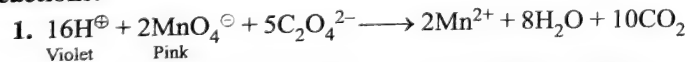
3.8.4 Self-Indicator in Redox Titration

Oxidising agents such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, and I_2 can be used as self-indicators in redox titration. In case of KMnO_4 , the colour changes from violet to pink in acidic medium due to the reduction of MnO_4^{\ominus} to Mn^{2+} .

In $\text{K}_2\text{Cr}_2\text{O}_7$, the colour changes from orange to green due to the reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} in acidic medium.

Similarly in I_2 , the colour changes from dark brown to colourless due to reduction of I_2 to I^{\ominus} .

Reactions:



However, in the titration of $\text{Cr}_2\text{O}_7^{2-}$ with a reducing agent such as $\text{C}_2\text{O}_4^{2-}$, both internal and external indicators are used. Diphenylamine + H_3PO_4 is used as an internal indicator, and at the end point, change in colour from green to bluish violet takes place, whereas potassium ferricyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$, is used as an external indicator, and at the end point, change in colour from blue to light brownish yellow takes place.

3.8.5 Determination of Alkalinity in a Given Water Sample

The alkalinity of water is its acid neutralising capacity. It is the sum of all the titrable bases. The alkalinity of natural water is due to the

salt of carbonates, bicarbonates, borates, silicates, and phosphates along with hydroxyl ions in the free state. However, the major portion of the alkalinity in natural water is caused by hydroxides, carbonates, and bicarbonates, which may be ranked in order of their association with high pH values. Alkalinity measurement is used in the interpretation and control of water and waste water treatment process.

Principle: The alkalinity of a sample can be estimated by titration with standard H_2SO_4 or HCl solution. Titration at pH = 8.3 or decolourisation of phenolphthalein indicator will indicate complete neutralisation of OH^{\ominus} and 1/2 of CO_3^{2-} , while at pH = 4.5 or sharp change from yellow to orange of methyl orange indicator will indicate total alkalinity (complete neutralisation of OH^{\ominus} , CO_3^{2-} , and HCO_3^{\ominus}).

ILLUSTRATION 3.68

20 mL of x M HCl neutralises completely 10 mL of 0.1 M NaHCO_3 solution and a further 5 mL of 0.2 M Na_2CO_3 to methyl orange end point. What is the value of x ?

Sol. mEq of HCl = mEq of NaHCO_3 + mEq of Na_2CO_3

$$20 \times x = 10 \times 0.1 + 5 \times 0.2 \times 2$$

$$x = \frac{3}{20} = 0.15 \text{ M}$$

ILLUSTRATION 3.69

How many mL of 0.1 N HCl is required to react completely using phenolphthalein with 2.0 g mixture of Na_2CO_3 and NaOH containing equimolar amounts of two?

Sol. Let x mol each of Na_2CO_3 and NaOH be there in 2.0 g mixture. So

$$x(106) + x(40) = 2 \Rightarrow x = \frac{1}{73}$$

In neutralisation:

$$\text{g Eq of } \text{Na}_2\text{CO}_3 = 2x$$

But only half will be neutralised in phenolphthalein.

$$\text{g Eq of } \text{NaOH} = x; \text{ fully neutralised}$$

$$\Rightarrow \frac{1}{2}(2x) + x = \text{g mEq of HCl} = \frac{1}{10} V$$

$$\Rightarrow 2x = \frac{V}{10}$$

$$\text{or } V = 20x = 20 \left(\frac{1}{73} \right) = 0.274 \text{ L} \approx 274 \text{ mL}$$

ILLUSTRATION 3.70

One gram of a mixture of NaHC_2O_4 and $\text{Na}_2\text{C}_2\text{O}_4$ dissolved in water consumes in titration 50.28 mL of 0.1 N NaOH with phenolphthalein as indicator. If 1 g of the mixture is heated to constant weight, what would be the weight of Na_2CO_3 produced?

Sol. The acid oxalate consumes 50.28 mL of 0.1 N NaOH
50.28 mL of 0.1 N NaOH

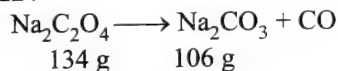
$$= \frac{50.28}{1000} \times 0.1 \text{ Eq} = 5.028 \times 10^{-3} \text{ Eq}$$

This reacts with the same quantity, i.e., 5.028×10^{-3} mol of $\text{NaHC}_2\text{O}_4 = (5.028 \times 10^{-3} \times 112) \text{ g} = 0.563 \text{ g}$

$$\therefore 1 - 0.563 = 0.437 \text{ g is } \text{Na}_2\text{C}_2\text{O}_4$$

Since $2\text{NaHC}_2\text{O}_4$ gives Na_2CO_3 , 0.563 g would give

$$\frac{0.563}{224} \times 106 \text{ g} = 0.2664 \text{ g of } \text{Na}_2\text{CO}_3$$



$$0.437 \text{ g would yield } \frac{0.437}{134} \times 106 = 0.3457 \text{ g of } \text{Na}_2\text{CO}_3$$

$$\therefore \text{Total weight of } \text{Na}_2\text{CO}_3 = 0.2664 + 0.3457 = 0.6121 \text{ g}$$

ILLUSTRATION 3.71

A mixture solution of KOH and Na_2CO_3 requires 15 mL of $N/20$ HCl when titrated with phenolphthalein as indicator. But the same amount of the solutions when titrated with methyl orange as indicator requires 25 mL of the same acid. Calculate the amount of KOH and Na_2CO_3 present in the solution.

Sol.

a. With methyl orange as indicator:

Full titre value of KOH (let x mEq) + Full titre value of

$$\text{Na}_2\text{CO}_3 (\text{let } y \text{ mEq}) = 25 \text{ mL} \times \frac{N}{20} \text{ mEq}$$

$$\therefore x + y = 25 \text{ mL} \times \frac{N}{20} \quad \dots(i)$$

b. With phenolphthalein as indicator:

$$\text{Full titre value of } \text{KOH} (x \text{ mEq}) + \frac{1}{2} \text{ titre value of}$$

$$\text{Na}_2\text{CO}_3 \left(\frac{y}{2} \text{ mEq} \right) = 15 \text{ mL} \times \frac{N}{20} \text{ mEq}$$

Solving Eqs. (i) and (ii), we get

$$x = \frac{1}{4} \text{ mEq}, y = 1 \text{ mEq.}$$

$$(Mw = Ew \text{ of } \text{KOH} = 56, Mw \text{ of } \text{Na}_2\text{CO}_3 = 106,$$

$$Ew = 106/2 = 53)$$

$$\text{mEq of HCl} = \text{mEq of } \text{Na}_2\text{CO}_3$$

$$= 1 \text{ mEq of } \text{Na}_2\text{CO}_3$$

$$= 1 \times 10^{-3} \times 53 \text{ g of } \text{Na}_2\text{CO}_3$$

$$= 0.053 \text{ g of } \text{Na}_2\text{CO}_3$$

$$\text{Similarly, mEq of HCl} = \text{mEq of KOH}$$

$$= \frac{1}{4} \times 10^{-3} \times 56 \text{ g of KOH}$$

$$= 0.014 \text{ g of KOH}$$

ILLUSTRATION 3.72

500 mL of a solution contains 2.65 g of Na_2CO_3 and 4 g of NaOH . 20 mL of this solution titrated each time against $N/10$ H_2SO_4 . Find out the titre value if

- Methyl orange is taken as an indicator
- Phenolphthalein is taken as indicator

Sol. Na_2CO_3 in 1 L = $2 \times 2.65 = 5.3 \text{ g}$

$$\text{NaOH in 1 L} = 2 \times 4 = 8 \text{ g}$$

$$\text{Normality of } \text{Na}_2\text{CO}_3 = \frac{5.3}{53} = 0.1 \text{ N}$$

$$\text{Normality of NaOH} = \frac{8}{40} = \frac{1}{5} \text{ N}$$

$$N_1 V_1 (\text{H}_2\text{SO}_4) = N_2 V_2 (\text{Na}_2\text{CO}_3)$$

$$\frac{N}{10} \times V_1 = 20 \times 0.1 \text{ N}$$

$$V_1 = 20 \text{ cc}$$

$$N_1 V_1 (\text{H}_2\text{SO}_4) = N_2 V_2 (\text{NaOH})$$

$$\frac{N}{10} \times V_1 = \frac{N}{5} \times 20$$

$$V_1 = \frac{1}{5} \times 20 \times 10 = 40 \text{ cc}$$

With methyl orange as an indicator:

$$\text{Full titre value of NaOH} + \text{Full titre value of } \text{Na}_2\text{CO}_3 = 40 + 20 = 60 \text{ cc}$$

With phenolphthalein as an indicator:

$$\text{Full titre value of NaOH} + \frac{1}{2} \text{ titre value of } \text{Na}_2\text{CO}_3 = 40 + 10 = 50 \text{ cc}$$

ILLUSTRATION 3.73

A solution contains Na_2CO_3 and NaHCO_3 . 10 mL of the solution required 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 were required. Calculate the amount of Na_2CO_3 and NaHCO_3 in 1 L of the solution.

Sol. Let $\text{Na}_2\text{CO}_3 = x$ mEq

and $\text{NaHCO}_3 = y$ mEq

are present in the solution.

a. With phenolphthalein as indicator:

Na_2CO_3 reacts to half its titre value and NaHCO_3 does not react.

$$\therefore \frac{x}{2} = 2.5 \text{ mL} \times 0.1 \times 2 \text{ N mEq of } \text{H}_2\text{SO}_4$$

$$\therefore x = 1 \text{ mEq of } \text{H}_2\text{SO}_4/10 \text{ mL}$$

('n' factor for $\text{H}_2\text{SO}_4 = 2$)

$$\begin{aligned} \text{mEq of } \text{H}_2\text{SO}_4 &= \text{mEq of } \text{Na}_2\text{CO}_3 \\ &= 1 \text{ mEq}/10 \text{ mL} \\ &= 1 \times 10^{-3} \text{ Eq}/10 \text{ mL} \\ &= \frac{10^{-3} \times 10^3}{10} \text{ Eq/L} \\ &= 0.1 \text{ Eq/L} \\ &= 0.1 \times 53 = 5.3 \text{ g} \end{aligned}$$

$$\left[\begin{array}{l} \text{'n' factor of } \text{Na}_2\text{CO}_3 = 2 \\ \text{Mw} = 106, \text{Ew} = \frac{106}{2} = 53 \end{array} \right]$$

b. With Methyl orange as indicator:

After the reaction using phenolphthalein as indicator, $\frac{1}{2}$ mEq of Na_2CO_3 and 1 mEq of NaHCO_3 is left in the solution.

$$\therefore \frac{x}{2} + y = 2.5 \text{ mL} \times 0.2 \times 2 \text{ N of } \text{H}_2\text{SO}_4$$

$$\therefore y = \frac{1}{2} \text{ mEq}$$

$$\begin{aligned} \text{mEq of } \text{H}_2\text{SO}_4 &= \text{mEq of } \text{NaHCO}_3 \\ &= \frac{1}{2} \text{ mEq}/10 \text{ mL} \\ &= \frac{1}{2} \times 10^{-3} \text{ Eq}/10 \text{ mL} \\ &= \frac{1}{2} \times \frac{10^{-3} \times 10^3}{10} \text{ Eq/L} \\ &= 0.05 \text{ Eq} \\ &= 0.05 \times \text{Ew of } \text{NaHCO}_3 \\ &= 0.05 \times 84 \\ &= 4.2 \text{ g/L} \end{aligned}$$

$$\left[\begin{array}{l} \text{'n' factor for } \text{NaHCO}_3 = 1 \\ \therefore \text{Mw} = \text{Ew of } \text{NaHCO}_3 = 84 \end{array} \right]$$

$$\text{N}_2 \text{ of } \text{NaHCO}_3 = 0.05 \text{ N}$$

$$\text{Amount of } \text{NaHCO}_3 \text{ in 1 L}$$

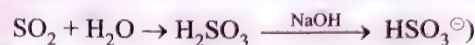
$$= 0.05 \times \text{Ew of } \text{NaHCO}_3$$

$$= 0.05 \times 84 = 4.2 \text{ g}$$

$$\left[\begin{array}{l} \text{'n' factor of } \text{NaHCO}_3 = 1 \\ \text{So Mw} = \text{Ew of } \text{NaHCO}_3 = 84 \end{array} \right]$$

ILLUSTRATION 3.74

A sample of fuming H_2SO_4 contains H_2SO_4 , SO_3 , and SO_2 . 2.0 g of the above sample was dissolved in water to make a 500 mL solution. 50 mL of the above solution on titration in presence of methyl orange requires 42.4 mL of 0.1 N NaOH. On the other hand, 100 mL of the same sample solution requires 1.85 mL of 0.1 N of I_2 where I_2 is reduced to I^\ominus ions. Determine the percentage composition of oleum sample. (In methyl orange,



Sol. NaOH displaces only one proton from H_2SO_3 obtained from SO_2 in methyl orange as indicator.

$$\text{Eq of } \text{SO}_2 = \text{Eq of } \text{H}_2\text{SO}_3$$

$$\text{Ew of } (\text{H}_2\text{SO}_3) = \frac{\text{Mw}}{x} \quad (x = 1)$$

Let x g of H_2SO_4 , y g of SO_3 , and z g of SO_2 in 2.0 g/500 mL mixture.

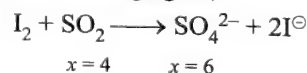
$$\text{i. } x + y + z = 2.0$$

ii. In 50 mL sample

$$\text{mEq of NaOH} = \text{mEq of } (\text{SO}_3 + \text{H}_2\text{SO}_4 + \text{SO}_2)$$

$$42.4 \times 0.1 = \left(\frac{x/10}{98/2} + \frac{y/10}{80/2} + \frac{z/10}{64/1} \right) \times 1000$$

iii. In 100 mL sample: only SO_2 reacts with I_2 (I_2 is used as oxidising agent)



$$\text{mEq of } \text{SO}_2 = \text{mEq of } \text{I}_2$$

$$1000 \left(\frac{z/5}{64/2} \right) = 1.85 \times 0.101$$

$$z = 0.0298 \text{ g}$$

$$\% \text{ of } z = \frac{0.0298}{2} \times 100 = 1.495 \%$$

From (ii)

$$\frac{x}{49} + \frac{y}{40} + \frac{z}{64} = 0.042$$

$$\text{Substituting } z = 0.0298$$

$$x = 1.60 \qquad \% x (\text{H}_2\text{SO}_4) = 80$$

$$y = 0.369 \qquad \% y (\text{SO}_3) = 1.85$$

$$z = 0.0298 \qquad \% z (\text{SO}_2) = 1.495$$

ILLUSTRATION 3.75

6.5 g mixture of sample containing KOH, NaOH, and Na_2CO_3 was dissolved in H_2O and the volume was made up to 250 mL. 25 mL of this solution requires 26.23 mL of 0.5 N H_2SO_4 using methyl orange as indicator, and 19.5 mL of same H_2SO_4 using phenolphthalein as indicator for complete neutralisation. Calculate the percentage of KOH, NaOH, and Na_2CO_3 in the sample.

Sol. Let a , b , and c mEq of H_2SO_4 is required for neutralisation of KOH, NaOH, and Na_2CO_3 by using methyl orange as indicator. So

$$a + b + c = 26.23 \text{ mL} \times 0.5 \text{ NH}_2\text{SO}_4 \quad \dots(i)$$

When phenolphthalein is used as indicator,

$$a + b + \frac{c}{2} = 19.5 \text{ mL} \times 0.5 \text{ NH}_2\text{SO}_4 \quad \dots(ii)$$

Solving Eqs. (i) and (ii), we get

$$a + b = 6.385 \text{ mEq}$$

$$c = 6.73 \text{ mEq}$$

$$\text{mEq of Na}_2\text{CO}_3 = 6.73 \text{ mEq of Na}_2\text{CO}_3$$

$$= 6.73 \times 10^{-3} \times \frac{106}{2} \text{ g} \text{ in } 25 \text{ mL}$$

$$= 0.357 \times \frac{250}{25} \text{ g} \text{ in } 250 \text{ mL}$$

$$= 3.57 \text{ g of Na}_2\text{CO}_3$$

$$\text{Percentage of Na}_2\text{CO}_3 = \frac{3.57}{6.5} \times 100 = 54.92\%$$

$$\text{Mass of (KOH + NaOH)} = 6.5 - 3.57 = 2.93 \text{ g}$$

Let x g of KOH and $(2.93 - x)$ g of NaOH

$$\therefore \left(\frac{x}{56} + \frac{2.93 - x}{40} \right) \times 1000 = 6.385 \times 10$$

$$\left[\begin{array}{l} \text{Since } a + b = 12.77 \text{ in } 25 \text{ mL of solution} \\ \text{In } 250 \text{ mL, } a + b = 6.385 \times 10 \end{array} \right]$$

$$\text{Solving } x = 1.316 \text{ g}$$

$$\% \text{ of KOH} = \frac{1.316}{6.5} \times 100 = 20.24\%$$

$$\% \text{ of NaOH} = 100 - (54.92 + 20.24) = 24.84\%$$

CONCEPT APPLICATION EXERCISE 3.6

Subjective Type

- 200 mL of a solution of a mixture of NaOH and Na_2CO_3 was first titrated with 0.1 M HCl using phenolphthalein indicator. 17.5 mL of HCl was required for the end point. After this methyl orange was added and 2.5 mL of the same HCl was again required for next end point. Find the amount of NaOH and Na_2CO_3 in the mixture.
- 30 mL of a solution of mixture of Na_2CO_3 and NaHCO_3 required 12 mL of 0.05 M H_2SO_4 using phenolphthalein as indicator. With methyl orange, 30 mL of the same solution required 40 mL of same H_2SO_4 . Calculate the amount of Na_2CO_3 and NaHCO_3 per litre in the mixture.
- 0.58 g of $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ was burnt in excess air and the resulting gases (CO_2 and H_2O) were passed through excess NaOH solution. The resulting solution was divided into two equal parts. One part requires 50 mL of 1.0 M HCl for complete neutralisation using phenolphthalein indicator. Another part required 80 mL of same HCl for neutralisation using methyl orange as indicator. Calculate the value of n and the amount of excess NaOH solution taken initially.
- Two drops of phenolphthalein was added to 40 mL of HCl solution. When 30 mL of 0.1 M NaOH was added, part

of the the solution turned pink, but colour disappeared on mixing the solution. Addition of NaOH was continued drop-wise until a one-drop addition produced a lasting pink colour, and the volume of NaOH added was 32.56 mL. Calculate

- The concentration of HCl solution
 - The concentration of HCl solution when 30 mL base was added
 - The pH of solution when 30 mL base was added
 - The pH of solution when 32.56 mL base was added
- 50 mL of a solution containing 1 g each of Na_2CO_3 , NaHCO_3 and NaOH was titrated with N HCl. What will be the titre value if:
 - Only phenolphthalein is used as an indicator?
 - Only methyl orange is used as an indicator from the very beginning?
 - Methyl orange is added after the first end point with phenolphthalein?
 - 1.7225 g of a metal (bivalent) salt $\text{A}_x(\text{CO}_3)_y(\text{OH})_z$ was dissolved in water to make 100 mL of solution. 50 mL of this solution required 10 mL of 0.5 M H_2SO_4 solution for complete neutralisation using phenolphthalein indicator. Another 50 mL solution required 15 mL of same acid using methyl orange indicator. Deduce the formula of the salt.

ANSWERS

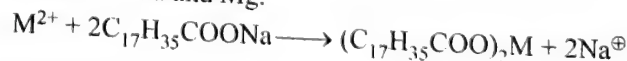
Subjective Type

- NaOH = 0.06 g., $\text{Na}_2\text{CO}_3 = 0.0265 \text{ g}$
- $\text{Na}_2\text{CO}_3 = 4.24 \text{ g L}^{-1}$, $\text{NaHCO}_3 = 4.48 \text{ g L}^{-1}$
- $n = 4$, Weight of NaOH = 3.2 g
- a. $M_{\text{HCl}} = 0.0814$, b. $M_{\text{HCl}} = 3.66 \times 10^{-3}$
c. pH = 2.4365 d. pH = 7
- a. $V_1 = 34.4 \text{ mL}$
b. $V_2 = 55.8 \text{ mL}$ c. $V_3 = 21.3 \text{ mL}$
- $\text{A}_3(\text{CO}_3)_2(\text{OH})_2$

3.9 HARD AND SOFT WATER

Water which produces lathers with soap is called soft water and which does not produce lather with soap is called hard water.

Hardness is due to the presence of bicarbonates, chlorides, and sulphates of Ca and Mg.



(M = Ca^{2+} , Mg^{2+}) Sodium stearate (soap)

Ca^{2+} or Mg^{2+} ions present in hard water react with soap to form a precipitate of Ca and Mg salts of fatty acids and hence no lather is produced.

3.9.1 Types of Hardness

Temporary hardness or carbonate hardness is due to the presence of soluble $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ and permanent or non-carbonate hardness is due to the presence of CaCl_2 , MgCl_2 , CaSO_4 .

and MgSO_4 . The process of removal of Ca^{2+} or Mg^{2+} ion is called softening of water.

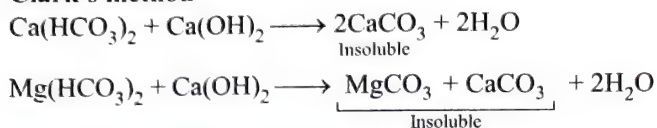
3.9.2 Removal of Hardness of Water

Removal of Temporary Hardness

a. By Boiling

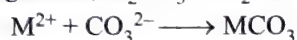


b. Clark's method

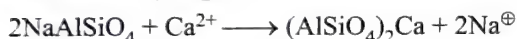


Removal of Permanent Hardness

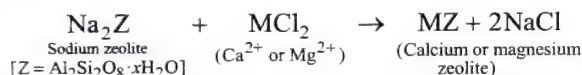
a. By washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)



b. Ion exchange method: (Inorganic cation exchangers) (*permutit method*). Permutit is an artificial zeolite, chemically it is sodium aluminium ortho silicates, $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ or $(\text{NaAlSiO}_4 \cdot 3\text{H}_2\text{O})$



or



The exhausted resin is regenerated by passing 10% solution of NaCl.

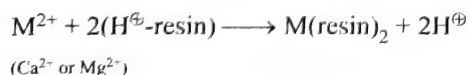


c. Organic ion exchanger

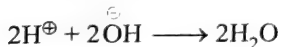
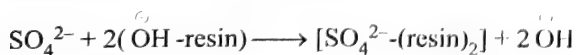
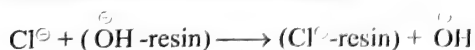
These are complex organic molecules having big molecules with either acidic group ($-\text{SO}_3\text{H}$ or $-\text{COOH}$) or basic

group (OH or NH_2) attached to them. Cation exchangers are capable of exchanging H^+ ions for cations and are represented by H^+ -resin, whereas the anion exchangers are capable of exchanging OH^- or NH_2^- ions for other anions and are represented as OH^- -resin

Reactions in cation exchanger:

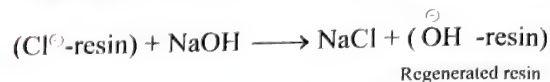


Reactions in anion exchanger



The water obtained by this method is free from all types of cations and anions and known as de-ionised or demineralised water.

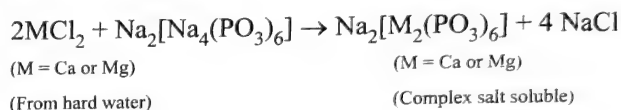
Regeneration of resins:



3.9.3 Internal Treatment of Hardness by Calgon Process (Sequestration)

In this process, Ca^{2+} and Mg^{2+} ions present in hard water are rendered ineffective (sequestered) by treatment with sodium polymetaphosphate (NaPO_3)_x, where x is as high as 100, or more commonly with sodium hexametaphosphate (NaPO_3)₆ or $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$. Its trade name is *calgon* (which means calcium gone).

When calgon is added to hard water, the Ca^{2+} and Mg^{2+} ions present in it combine with $(\text{NaPO}_3)_6$ to form a soluble complex of Ca and Mg salts.



The complex Ca and Mg ions do not form any precipitate with soap and hence readily produce lather with soap solution.

Hard water is harmful to steam boilers due to the formation of *boiler scale* (CaSO_4 , CaCO_3 , and MgOCl). It reduces the efficiency of the boiler and damages it.

3.9.4 Units of Hardness

Degree of Hardness of Water in Terms of Parts Per Million or (ppm)

Concentration of solute (in ppm) = mass of solute in gram in 10^6 mL solution.

It is used in determining the *hardness of water* due to the presence of bicarbonates (temporary hardness), chlorides and sulphates (permanent hardness) of calcium and magnesium.

The degree of hardness is defined as the number of parts of CaCO_3 or equivalent to other Ca and Mg salts present in a million (10^6) parts of water.

$$\text{Ew}(\text{CaCO}_3) = \frac{100}{2} = 50$$

$$\text{Ew}(\text{MgSO}_4) = \frac{120}{2} = 60$$

$$\text{Ew}(\text{CaCl}_2) = \frac{111}{2} = 55.5$$

$$\begin{aligned} \text{This means } 50 \text{ g of } \text{CaCO}_3 &\equiv 60 \text{ g of } \text{MgSO}_4 \\ &\equiv 55.5 \text{ g of } \text{CaCl}_2 \end{aligned}$$

For example:

1. Degree of hardness in a water sample containing 222 ppm of CaCl_2

$$55.5 \text{ g } \text{CaCl}_2 \equiv 50 \text{ g of } \text{CaCO}_3$$

$$222 \text{ g CaCl}_2 \equiv \frac{50 \times 222}{55.5} = 200 \text{ ppm}$$

2. Degree of hardness in a water sample containing 36 mg of MgSO_4 per kg of water

$$10^3 \text{ mL or } 10^3 \text{ g H}_2\text{O contains MgSO}_4 = 36 \text{ mg}$$

$$10^6 \text{ g H}_2\text{O contains MgSO}_4 = 36 \times 10^3 \text{ mg} = 36 \text{ g}$$

From the formula

$$1 \text{ mol of MgSO}_4 \equiv 1 \text{ mol of CaCO}_3$$

$$120 \text{ g of MgSO}_4 \equiv 100 \text{ g of CaCO}_3$$

$$36 \text{ g of MgSO}_4 = \frac{100 \times 36}{120} = 30 \text{ g of CaCO}_3$$

$$\therefore \text{Degree of hardness} = 30 \text{ ppm}$$

Hardness in Terms of CaCO_3 Equivalents

The reason of expressing hardness as CaCO_3 equivalents is due to the fact that its molecular mass is $40 + 12 + 48 = 100$ (or equivalent weight = 50) and it is the most insoluble salt that can be precipitated in water treatment.

Eq of CaCO_3

$$\begin{aligned} & \frac{\text{Mass of hardness producing material}}{\times \text{Chemical Eq of CaCO}_3} \\ &= \frac{\text{Chemical Eq of hardness producing substance}}{\text{Mass of hardness producing substance} \times 50} \\ &= \frac{\text{Chemical Eq of hardness producing substance}}{\text{Chemical Eq of hardness producing substance}} \end{aligned}$$

For example, the molecular mass of $\text{Ca}(\text{HCO}_3)_2$ is 162 and that of CaCO_3 is 100. So $\text{CaCO}_3:\text{Ca}(\text{HCO}_3)_2 = 100 : 162$. The chemical equivalent of $\text{Ca}(\text{HCO}_3)_2$ is $162/2 = 81$. In other words, 162 parts by mass of $\text{Ca}(\text{HCO}_3)_2$ or 2 Eq react with same amounts as 100 parts by mass of CaCO_3 of 2 Eq. The $\text{Ca}(\text{HCO}_3)_2$ expressed as CaCO_3 Eq can be written as:

$$162 \times \frac{100}{162} = 100 \text{ Eq of CaCO}_3$$

Similarly	Factor
$\text{CaSO}_4:\text{CaCO}_3 = 136:100$	$100/136$
$\text{CaCl}_2:\text{CaCO}_3 = 111:100$	$100/111$
$\text{MgCl}_2:\text{CaCO}_3 = 95:100$	$100/95$
$\text{MgSO}_4:\text{CaCO}_3 = 120:100$	$100/120$
$\text{MgCO}_3:\text{CaCO}_3 = 84:100$	$100/84$

It should be noted that chemical equivalents of CaCO_3 , CaSO_4 , CaCl_2 , MgCl_2 , MgSO_4 , and MgCO_3 , are 50, 68, 55.5, 47.5, 60, and 42, respectively.

$$1 \text{ ppm} = \frac{1 \text{ part of hardness}}{10^6 \text{ parts of water}}$$

- Note:**
- If the dissolved salts of Ca^{2+} and Mg^{2+} (including bicarbonates) causing hardness are present in water to the extent of 50–100, 100–250 and above 250 ppm of CaCO_3 equivalent, then the water is called not too hard, hard, and very hard respectively.
 - The degree of hardness upto 100–150 ppm in water required for our daily needs such as cooking and bathing, washing of clothes, etc., is tolerable. But if the degree of hardness exceeds this limit then water is not suitable for domestic use.

ILLUSTRATION 3.77

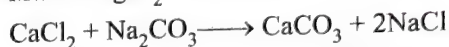
A sample of hard water contains 1 mg CaCl_2 and 1 mg MgCl_2 per litre. Calculate the hardness of water in terms of CaCO_3 present in per 10^6 parts of water.

- a. 2.5 ppm b. 1.95 ppm c. 2.15 ppm d. 195 ppm

Sol. M_w of $\text{CaCl}_2 = 111.0 \text{ g}$

$$M_w = \text{CaCO}_3 = 100 \text{ g}$$

$$M_w \text{ of MgCl}_2 = 95.0 \text{ g}$$



i. $111.0 \text{ g CaCl}_2 \equiv 100 \text{ g CaCO}_3$

$$1 \text{ mg CaCl}_2 \equiv \frac{100}{111} \text{ mg CaCO}_3 = 0.9 \text{ mg CaCO}_3$$

ii. $95.0 \text{ g MgCl}_2 \equiv 100 \text{ g CaCO}_3$

$$1 \text{ mg MgCl}_2 \equiv \frac{100}{95} \text{ mg CaCO}_3 = 1.05 \text{ mg CaCO}_3$$

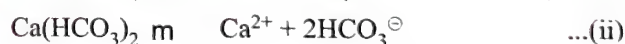
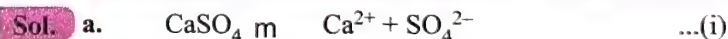
Hardness of CaCO_3 ppm

$$\begin{aligned} &= \frac{(0.9 + 1.05) \times 10^{-3} \text{ g} \times 10^6 \text{ mL}}{10^3 \text{ mL}} \\ &= 1.95 \text{ ppm} \end{aligned}$$

ILLUSTRATION 3.76

A water sample is found to contain 96 ppm of SO_4^{2-} and 122 ppm of HCO_3^- with Ca^{2+} ion as the only cation.

- Calculate the ppm of Ca^{2+} in water.
- Calculate the mol of CaO required to remove HCO_3^- ion from 1000 kg of the water.
- Calculate the concentration of Ca^{2+} in ppm remaining in water after adding CaO .



i. $96 \text{ ppm of SO}_4^{2-} = 96 \text{ g SO}_4^{2-} \text{ in } 10^6 \text{ mL H}_2\text{O}$
 $(M_w \text{ of SO}_4^{2-} = 96 \text{ g})$

$$= \frac{96}{96} \text{ mol of SO}_4^{2-} / 10^6 \text{ mL H}_2\text{O}$$

$$= 1 \text{ mol of SO}_4^{2-} / 10^6 \text{ mL H}_2\text{O}$$

$$= 1 \text{ mol of Ca}^{2+} / 10^6 \text{ mL H}_2\text{O}$$

ii. $122 \text{ ppm of HCO}_3^- \equiv 122 \text{ g HCO}_3^- \text{ in } 10^6 \text{ mL H}_2\text{O}$
 $(M_w \text{ of HCO}_3^- = 61 \text{ g})$

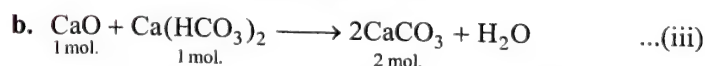
$$\equiv \frac{122}{61} = 2 \text{ mol of HCO}_3^-$$

$$\equiv 1.0 \text{ mol of Ca}^{2+}$$

[Since 1 mol. of $\text{Ca}(\text{HCO}_3)_2 = 2 \text{ mol. of HCO}_3^-$]

$$\text{Total Ca}^{2+} = 1 + 1 = 2 \text{ mol of Ca}^{2+} = 80 \text{ g in } 10^6 \text{ mL H}_2\text{O}$$

$$\boxed{\text{ppm Ca}^{2+} = 80}$$



$$= 2 \text{ mol HCO}_3^- \text{ in } 10^6 \text{ g H}_2\text{O}$$

2 mol of HCO_3^- is present in $10^6 \text{ mL} (= 10^6 \text{ g}) = 1000 \text{ kg}$ of H_2O .

From Eq. (iii), 1 mol of CaO is required to remove 2 mol of HCO_3^- present in 1000 kg of H_2O .

c. Total Ca^{2+} already present = 2 mol

Ca^{2+} removed in Eq. (iii) = 1 mol

Thus Ca^{2+} (left) = $2 - 1 = 1 \text{ mol} = 40 \text{ g} = 400 \text{ ppm}$

From Eq. (iii), it is clear that HCO_3^- ions are removed as CaCO_3 , but SO_4^{2-} ions are left in the solution.

ILLUSTRATION 3.78

Hardness of water is 200 ppm. The normality and molarity of CaCO_3 in the water is

a. $2 \times 10^{-6} \text{ N}, 2 \times 10^{-6} \text{ M}$

b. $4 \times 10^{-2} \text{ N}, 2 \times 10^{-2} \text{ M}$

c. $4 \times 10^{-3} \text{ N}, 2 \times 10^{-3} \text{ M}$

d. $4 \times 10^{-1} \text{ N}, 2 \times 10^{-1} \text{ M}$

Sol. c. Hardness is weight in grams of CaCO_3 in 10^6 mL of H_2O or 10^6 g of H_2O ($\because d \text{H}_2\text{O} = 1$)

$$M_w(\text{CaCO}_3) = 100 \text{ g mol}^{-1}$$

$$M = \frac{W_2 \times 1000}{M_w \times \text{Volume of solution in mL}}$$

$$= \frac{200 \times 1000}{100 \times 10^6} = 2 \times 10^{-3} \text{ M}$$

$$N = n \times M = 2 \times 2 \times 10^{-3} = 4 \times 10^{-3} \text{ N}$$

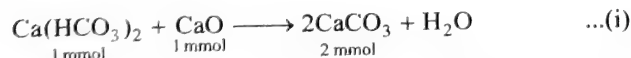
ILLUSTRATION 3.79

A sample of hard water contains 122 ppm of HCO_3^- ions. What is the minimum weight of CaO required to remove ions completely from 1 kg of such water sample?

a. 56 mg b. 112 mg c. 168 mg d. 244 mg

Sol. a. [$M_w \text{HCO}_3^- = 61 \text{ g}, M_w(\text{CaO}) = 56 \text{ g}$]

Temporary hardness is due to the HCO_3^- of Ca^{2+} and Mg^{2+} and is removed by either boiling or by treating with CaO or Ca(OH)_2 (Clark's method)



$$122 \text{ ppm of } \text{HCO}_3^- \equiv 122 \text{ g } \text{HCO}_3^- \text{ in } 10^6 \text{ mL or } 10^3 \text{ L}$$

$$\equiv 122 \text{ mg } \text{HCO}_3^- \text{ in } 1.0 \text{ L}$$

$$\equiv \frac{122}{61} = 2 \text{ mmol in } 1.0 \text{ L}$$

$$\equiv \frac{2}{2} \text{ n-factor} = 2$$

$$= 1 \text{ mmol of } \text{Ca(HCO}_3)_2 \text{ in } 1.0 \text{ L}$$

According to Eq. (i),

$$1 \text{ mmol of } \text{Ca(HCO}_3)_2 \equiv 1 \text{ mmol of } \text{CaO} \text{ in } 1.0 \text{ L}$$

$$\equiv 1 \times 56 \equiv 56 \text{ mg of } \text{CaO}$$

$$\equiv 56 \text{ mg of } \text{CaO} \text{ in } 1.0 \text{ L}$$

$$\equiv 56 \text{ mg of } \text{CaO} \text{ in } 1 \text{ kg of } \text{H}_2\text{O}$$

$$(1 \text{ L of } \text{H}_2\text{O} = 1 \text{ kg of } \text{H}_2\text{O}, \therefore d \text{H}_2\text{O} = 1)$$

ILLUSTRATION 3.80

100 mL samples of distilled water, tap water, and boiled water required, respectively, 2 mL, 17 mL, and 7 mL of soap solution to form permanent lather. The ratio of permanent to temporary hardness in the tap water is

a. 3:2

b. 2:3

c. 1:2

d. 2:1

Sol. c.

	Distilled H_2O	Tap H_2O	Boiled H_2O [Only permanent hardness; temporary hardness is removed by boiling]
	[No hardness, lather factor]	[Temporary + permanent hardness]	
Volume of soap solution required	2 mL	17 mL	7 mL
Volume of soap effectively used	—	$17 - 2 = 15 \text{ mL}$	$7 - 2 = 5 \text{ mL}$

(Temporary and permanent hardness) in tap $\text{H}_2\text{O} = 15 \text{ mL}$

Permanent hardness in boiled $\text{H}_2\text{O} = 5 \text{ mL}$

Temporary hardness in $\text{H}_2\text{O} = 15 - 5 = 10 \text{ mL}$

$$\frac{\text{Permanent hardness}}{\text{Temporary hardness}} = \frac{5}{10} = 1:2$$

Hence, answer is (c).

ILLUSTRATION 3.81

50 mL of water on titration with standard soap solution gave the following results: Lather factor = 0.4 mL, total hardness (TH) = 8.2 mL, permanent hardness (PH) = 2.5 mL and standard hard water (containing $0.2 \text{ g } \text{CaCO}_3 \text{ L}^{-1}$) = 19.9 mL. Calculate each type of hardness in ppm.

Sol. Strength of CaCO_3 in hard water

$$= \frac{0.2 \times 50}{1000} \text{ g L}^{-1} [E_w(\text{CaCO}_3) = 50]$$

$$= 0.01 \text{ g} = 10 \text{ mg of } \text{CaCO}_3 \text{ Eq}$$

Deducting lather factor,

$$\text{TH} = 8.2 - 0.4 = 7.8 \text{ mL}$$

$$\text{PH} = 2.5 - 0.4 = 2.1 \text{ mL}$$

Volume of soap solution corresponding to 50 mL of standard hard water = $19.9 - 0.4 = 19.5 \text{ mL}$

$$\therefore 19.5 \text{ mL of soap solution} \equiv 10 \text{ mg CaCO}_3 \text{ Eq}$$

$$1 \text{ mL of soap solution} = \frac{10}{19.5}$$

$$= 0.5128 \text{ mg CaCO}_3 \text{ Eq}$$

Volume of soap solution for total hardness

$$= 7.8 \text{ mL}$$

$$= 7.8 \times 0.5128 \text{ mg CaCO}_3 \text{ equivalents}$$

$$= \frac{7.8 \times 0.5128 \times 10^3 \text{ mL}}{50 \text{ mL}}$$

$$= 80 \text{ mg L}^{-1} = 80 \text{ ppm (80 g } 10^6 \text{ mL)}$$

$$\therefore \text{TH} = 80 \text{ ppm}$$

Volume of soap solution for PH

$$= 2.1 \text{ mL}$$

$$= 2.1 \times 0.5128 \text{ mg}$$

$$= \frac{2.1 \times 0.5128 \times 10^3 \text{ mL}}{50 \text{ mL}}$$

$$= 21.53 \text{ mg L}^{-1} = 21.53 \text{ g/} 10^6 \text{ mL}$$

$$= 21.53 \text{ ppm}$$

$$\text{Hence, PH} = 21.53 \text{ ppm}$$

$$\text{TH} = 80 - 21.53 = 58.47 \text{ ppm}$$

CONCEPT APPLICATION EXERCISE 3.7

Subjective Type

1. If water contains 10 ppm of MgCl_2 and 8 ppm of CaSO_4 , calculate the ppm of CaCO_3 .
2. Calculate the quantity of lime required to soften 10^3 L of H_2O which contains 7.5 g L^{-1} of $\text{Ca}(\text{HCO}_3)_2$ and 5.0 g L^{-1} of $\text{Mg}(\text{HCO}_3)_2$.
3. A 200 mL sample of water requires 5 mL of $\text{N}/20 \text{ Na}_2\text{CO}_3$ solution for complete precipitation of Ca^{2+} and CaCO_3 . Calculate the hardness in ppm.

ANSWERS

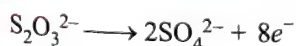
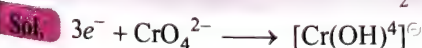
Subjective Type

1. 16.45
2. $8.48 \times 10^3 \text{ g}$
3. 62.5 ppm

Solved Examples

EXAMPLE 3.1

In basic solution CrO_4^{2-} oxidises $\text{S}_2\text{O}_3^{2-}$ to form $[\text{Cr}(\text{OH})_4]^-$ and SO_4^{2-} . How many millilitres of $0.154 \text{ M Na}_2\text{CrO}_4$ are required to react with 40.0 mL of $0.246 \text{ M Na}_2\text{S}_2\text{O}_3$.



$$N_1V_1 = N_2V_2$$

$$3 \times 0.154 \times V_1 = 8 \times 0.246 \times 40$$

$$\therefore V_1 = 170 \text{ mL}$$

EXAMPLE 3.2

600 mL of HNO_3 and 200 mL of $\text{Ca}(\text{OH})_2$ of same molarity are mixed to give a resulting solution having $\text{pH} = 1$. What is the molarity of HNO_3 and $\text{Ca}(\text{OH})_2$?

Sol. Let M be the molarity of HNO_3 and $\text{Ca}(\text{OH})_2$

$$\therefore \text{Normality of } \text{HNO}_3 = M \times 1 = M$$

$$\text{mEq of } \text{HNO}_3 = 600 \times M$$

$$\text{mEq of } \text{Ca}(\text{OH})_2 = 200 \times 2 \times M = 400 M$$

$$\text{After reaction, mEq of acid left} = (600 - 400) M = 200 M$$

$$\text{Total volume} = 600 + 200 = 800 \text{ mL}$$

$$\text{Normality of acid} = 200 M / 800 = M/4$$

$$\text{pH} = 1$$

$$\therefore [\text{H}^+] = 10^{-1}$$

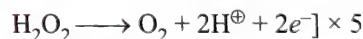
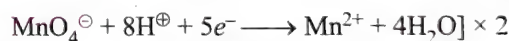
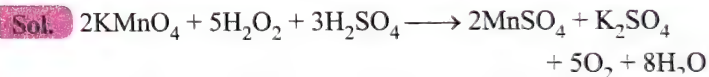
$$\therefore M/4 = 10^{-1} \therefore M = 0.4$$

$$\text{N of } \text{Ca}(\text{OH})_2 = 0.4 \times 2 = 0.8 \text{ N}$$

EXAMPLE 3.3

20 mL of a solution containing 0.2 g of an impure sample of H_2O_2 reacts with 0.316 g of KMnO_4 in the presence of H_2SO_4 .

- Find out the purity of H_2O_2 .
- Calculate the volume of dry oxygen evolved at 27°C and 750 mm Hg pressure.



$$\text{Ew (KMnO}_4) = 31.6$$

$$\text{Eq of KMnO}_4 = 0.316 / 31.6 = 10^{-2} \text{ Eq}$$

$$\therefore \text{Eq of } \text{H}_2\text{O}_2 = 10^{-2}$$

$$\text{Amount of } \text{H}_2\text{O}_2 = 10^{-2} \times 17 = 0.17 \text{ g}$$

$$\text{Purity of } \text{H}_2\text{O}_2 = \frac{0.17}{0.2} \times 100 = 85\%$$

$$\text{Eq of } \text{H}_2\text{O}_2 = \text{Eq of KMnO}_4 = \text{Eq of O}_2 = 10^{-2} \text{ Eq}$$

Since O_2 is obtained from both H_2O_2 and KMnO_4 ,

$$\text{Eq of O}_2 = 2 \times 10^{-2}$$

$$4 \text{ Eq of O}_2 = 1 \text{ mol} = 22400 \text{ mL at STP}$$

$$2 \times 10^{-2} \text{ Eq of O}_2 = \frac{22400}{4} \times 2 \times 10^{-2}$$

$$= 11200 \times 10^{-2} = 112 \text{ mL at STP}$$

Volume of O_2 at 27°C and 750 mm Hg pressure

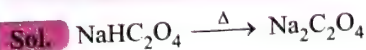
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{760 \times 112}{273} = \frac{750 \times V_2}{300}$$

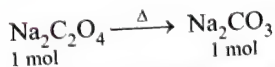
$$V_2 = \frac{760 \times 112 \times 300}{750 \times 273} = 124.7 \text{ mL}$$

EXAMPLE 3.4

10 g of a mixture of NaHC_2O_4 and $\text{Na}_2\text{C}_2\text{O}_4$ on heating gave 6.12 g of Na_2CO_3 . Another 10 g of the mixture was dissolved in 1.0 L of solution. 25 mL of this solution was titrated with 0.1 N NaOH. Find the volume of NaOH required.

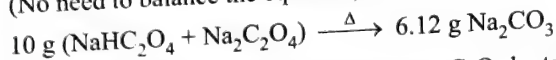


$$1 \text{ mol} \qquad \qquad \frac{1}{2} \text{ mol}$$



$$1 \text{ mol} \qquad \qquad 1 \text{ mol}$$

(No need to balance the equation)



Let x g of NaHC_2O_4 and $(10 - x)$ g of $\text{Na}_2\text{C}_2\text{O}_4$ be taken.

$$\frac{1}{2} \left(\frac{x}{112} \right) + \left(\frac{10 - x}{134} \right) = \frac{6.12}{106}$$

Solving, we get $x = 5.63$ g (NaHC_2O_4)

$$\therefore 10 - 5.63 = 4.37 \text{ g of } \text{Na}_2\text{C}_2\text{O}_4$$

Second experiment: NaOH reacts only with NaHC_2O_4 due to the presence of one acidic H atom only.

$$Ew (\text{NaHC}_2\text{O}_4) \equiv \frac{Mw}{1}$$

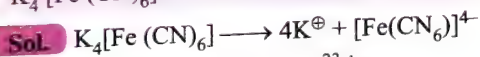
$$mEq \text{ of NaOH} = mEq \text{ of } \text{NaHC}_2\text{O}_4$$

$$V \times 0.1 \text{ N} \equiv \left(\frac{5.63}{112/1} \right) \times 1000 \times \frac{25}{1000}$$

$$V = 12.5 \text{ mL}$$

EXAMPLE 3.5

How many ions are present in 2.0 L of a solution that is 0.8 M $\text{K}_4[\text{Fe}(\text{CN})_6]$

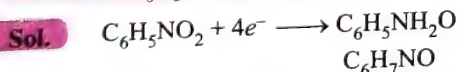


$$5 \text{ ions (mol)} = 5 \times 6 \times 10^{23} \text{ ions}$$

$$\text{Number of ions} = 5 \times 6 \times 10^{23} \times 0.8 \times 2 = 48 \times 10^{24} \text{ ions}$$

EXAMPLE 3.6

What is the charge involved when 0.1 mol of $\text{C}_6\text{H}_5\text{NO}_2$ is reduced to $\text{C}_6\text{H}_5\text{NHOH}$?



$$4 \times 6 + 5 + x - 4 = 0$$

$$x = -25$$

$$24 + 7 + x - 2 = 0$$

$$x = -29$$

$$n = -25 - (-29) = 4$$

$$1 \text{ mol} = 4 \text{ F or } 0.1 \text{ mol} = 0.4 \text{ F}$$

EXAMPLE 3.7

1.0 g of metal nitrate gave 0.86 g of metal carbonate. Calculate the equivalent weight of metal.

Sol. Let the equivalent weight of metal = E

$$Ew \text{ of metal nitrate} = Ew \text{ of } M + Ew \text{ NO}_3^- = E + 62$$

$$\text{Equivalent weight of metal carbonate}$$

$$= \text{Equivalent weight of Metal}$$

$$+ \text{Equivalent weight of } \text{CO}_3^{2-}$$

$$= E + \frac{60}{2} = E + 30$$

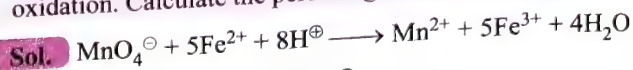
$$\therefore \frac{Ew \text{ of M nitrate}}{Ew \text{ of M carbonate}} = \frac{\text{Weight of M nitrate}}{\text{Weight of M sulphate}}$$

$$\frac{E + 62}{E + 30} = \frac{1.0}{0.86}$$

$$\therefore E = 166.57$$

EXAMPLE 3.8

0.804 g of Fe ore was dissolved in acid. Iron was reduced to +2 state and it required 47.2 mL of 0.112 N KMnO_4 for complete oxidation. Calculate the percentage of Fe and Fe_3O_4 in the ore.



$$47.2 \text{ mL of } 0.112 \text{ N } \text{KMnO}_4$$

$$= 47.2 \times 0.112 \text{ mEq of Fe}^{2+}$$

$$= 5.29 \times 10^{-3} \times 56 \text{ g of Fe}^{2+}$$

$$= 0.296 \text{ g of Fe}$$

$$\% \text{ of Fe} = \frac{0.296 \times 100}{0.804} = 36.82 \%$$

$$3 \text{ Fe} = \text{Fe}_3\text{O}_4$$

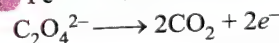
$$3 \times 56 \text{ g} = 3 \times 56 + 64$$

$$\therefore 168 \text{ g of Fe} = 232 \text{ g of } \text{Fe}_3\text{O}_4$$

$$\% \text{ of } \text{Fe}_2\text{O}_3 = \frac{232}{168} \times 36.8 = 50.85 \%$$

EXAMPLE 3.9

What volume of 0.1 M KMnO_4 is needed to oxidise 100 mg of ferrous oxalate in acidic medium?



$$Ew (\text{Fe}_2\text{C}_2\text{O}_4) = \frac{\text{Molecular weight}}{3} = \frac{56 + 88}{3} = 48$$

$$100 \text{ mL of } \text{FeC}_2\text{O}_4 = \frac{100 \times 10^{-3}}{48} = \frac{0.1}{48} \text{ Eq}$$

$$0.1 \text{ M } \text{KMnO}_4 = 0.5 \text{ N } \text{KMnO}_4 \text{ (} n \text{ factor} = 5 \text{)}$$

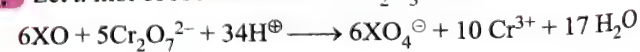
$$V \text{ mL of } 0.5 \text{ N } \text{KMnO}_4 = \frac{0.1}{48} \times 10^3 \text{ mEq of } \text{FeC}_2\text{O}_4$$

$$\therefore V \times 0.5 = \frac{0.1}{48} \times 10^{-3} = 4.17 \text{ mL}$$

EXAMPLE 3.10

You are given a 2.18 g sample containing a mixture of XO and X_2O_3 . It takes 0.015 mol of $\text{K}_2\text{Cr}_2\text{O}_7$ to oxidise the sample completely to form XO_4^- and Cr^{3+} . If 0.0187 mol of XO_4^- is formed, what is the atomic mass of X?

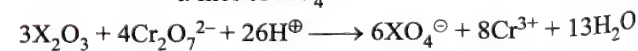
Sol. Let a mol of XO and b mol of X_2O_3 react.



$$6 \text{ mol of XO} = 5 \text{ mol of } \text{Cr}_2\text{O}_7^{2-} = 6 \text{ mol of } \text{XO}_4^-$$

$$a \text{ mol of XO} = \frac{5}{6} a \text{ mol of } \text{Cr}_2\text{O}_7^{2-}$$

$$= a \text{ mol of } \text{XO}_4^-$$



$$3 \text{ mol of } \text{X}_2\text{O}_3 = 4 \text{ mol of } \text{Cr}_2\text{O}_7^{2-} = 6 \text{ mol of } \text{XO}_4^-$$

$$b \text{ mol of } X_2O_3 = \frac{4}{3} b \text{ mol of } Cr_2O_7^{2-} \\ = 2b \text{ mol of } XO_4^{\ominus}$$

$$\therefore \frac{5a}{6} + \frac{4b}{3} = 0.015$$

$$a + 2b = 0.0187$$

$$\therefore a = 0.0152, b = 0.00175$$

Let the atomic weight of X be = m

Molecular weight of $XO = m + 16$

Molecular weight of $X_2O_3 = 2m + 48$

Weight of $XO = 0.0152(m + 16)$

Weight of $X_2O_3 = 0.00175(2m + 48)$

Total weight = 2.18

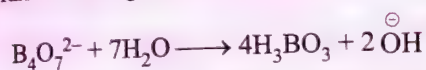
$$\therefore 0.0152(m + 16) + 0.00175(2m + 48) = 2.18$$

$$\therefore m = 99.08$$

$$\therefore \text{Atomic weight} = 99.08$$

EXAMPLE 3.11

Borax in water gives the following:

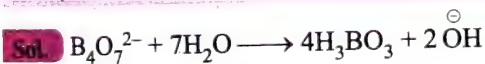


How many grams of borax ($Na_2B_4O_7 \cdot 10H_2O$) are required to

a. Prepare 50 mL of 0.2 M solution

b. Neutralise 25 mL of 0.2 M H_2SO_4

(Mw of borax = 382)



So, borax is a diacidic base.

a. millimoles = $\frac{\text{Weight}}{Mw} \times 1000$

$$\Rightarrow 50 \times 0.2 = \frac{\text{Weight}}{382} \times 1000 \Rightarrow \text{Weight} = 3.82 \text{ g}$$

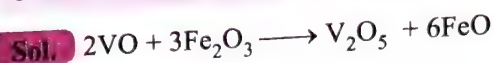
b. $\text{mEq} = \frac{\text{Weight}}{E} \times 1000 \Rightarrow 2 \times 0.2 \times 25$

$$= \frac{\text{Weight}}{382/2} \times 1000$$

$$\text{Weight} = 1.91 \text{ g}$$

EXAMPLE 3.12

In the reaction of vanadium oxide (VO) with iron oxide (Fe_2O_3), the products are V_2O_5 and FeO . How many grams of V_2O_5 can be formed from 2.00 g of VO and 5.75 g of Fe_2O_3 .



$$2 \text{ mol} : 3 \text{ mol} \qquad 1 \text{ mol} : 6 \text{ mol}$$

Here Fe_2O_3 is a limiting reagent.

$$3 \text{ mol of } Fe_2O_3 \equiv 1 \text{ mol of } V_2O_5$$

$$\frac{5.75}{160} = 0.036 \text{ mol of } Fe_2O_3 = \frac{0.036}{3} \text{ mol of } V_2O_5$$

$$\therefore \text{grams of } V_2O_5 = \frac{0.036}{3} \times 181.9 = 2.182 \text{ g}$$

EXAMPLE 3.13

A mixture of aluminium and Zn weighing 1.67 g was completely dissolved in acid, which evolved 1.69 L of H_2 at STP. What was the weight of aluminium in the original mixture.

Sol. Let the weight of Al be x g and weight of Zn be $(1.67 - x)$ g.

$$\text{Eq of Al} = \frac{x}{27/3},$$

$$\text{Eq of Zn} = \frac{(1.67 - x)}{65.4/2}$$

$$\text{Eq of } H_2 = \frac{1.69}{11.2}$$

$$\therefore \frac{x}{27/3} + \frac{(1.67 - x)}{65.4/2} = \frac{1.69}{11.2}$$

$$3 \times 65.4x + 1.67 \times 2 \times 27 - 2x \times 27 = \frac{1.69}{11.2} \times 27 \times 65.4$$

$$196.2x - 90.18 - 54x = 266.446$$

$$142.2x = 176.2666$$

$$\therefore x = 1.239 \text{ g}$$

Exercises

Single Correct Answer Type

- 34 g of H_2O_2 is present in 1120 mL of solution. This solution is called
(1) 10 vol solution (2) 20 vol solution
(3) 34 vol solution (4) 32 vol solution
- A 5.0 mL solution of H_2O_2 liberates 1.27 g of iodine from an acidified KI solution. The percentage strength of H_2O_2 is
(1) 11.2 (2) 5.6 (3) 1.7 (4) 3.4
- In Q. 2, the strength of H_2O_2 in terms of volume strength is
(1) 11.2 (2) 5.6 (3) 1.7 (4) 3.4
- If 20 mL of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ is required to titrate 10 mL of a liquid iron supplement, then the concentration of iron in the the the vitamin solution is
(1) 1.2 M (2) 2.4 M (3) 0.6 N (4) 1.56 M
- If an ore sample containing Mn is treated with 50 mL of 0.2750 M $\text{Na}_2\text{C}_2\text{O}_4$ and the unreacted $\text{Na}_2\text{C}_2\text{O}_4$ required 18.28 mL of 0.1232 M KMnO_4 in acidic medium, the number of moles of Mn in the ore is
(1) 1.38×10^{-2} (2) 1.49×10^{-3}
(3) 1.15×10^{-2} (4) 8.12×10^{-3}
- After 20 mL of 0.1 M $\text{Ba}(\text{OH})_2$ is mixed with 10 mL of 0.2 M HClO_4 , the concentration of OH^- ions is
(1) 2×10^{-3} M
(2) 10^{-3} M
(3) 0.066 M
(4) OH^- ions are completely neutralised.
- K_2CrO_4 oxidises KI in the presence of HCl to I_2 . The equivalent weight of the K_2CrO_4 is
(1) $\frac{M_w}{2}$ (2) $M_w \times \frac{2}{3}$ (3) $\frac{M_w}{3}$ (4) $\frac{M_w}{6}$
- The pH of 10^{-5} M HCl solution if 1 mL of it is diluted to 1000 mL is
(1) 5 (2) 8 (3) 7.02 (4) 6.98
- What volume of 0.1 M KMnO_4 is needed to oxidise 5 mg of ferrous oxalate in acidic medium (M_w of ferrous oxalate is 144.)
(1) 0.20 mL (2) 0.1 mL (3) 0.4 mL (4) 2.08 mL
- 4 mol of a solution, containing A^{n+} requires 1.6 mol of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. The value of n is
(1) 1 (2) 2 (3) 3 (4) 4
- One mole of N_2H_4 losses 10 mol of electrons to form a new compound A. Assuming that all nitrogen appears in the new compound, what is the oxidation state of nitrogen in A? There is no change in the oxidation state of hydrogen.
(1) +1 (2) -3 (3) +3 (4) +5
- 100 mL of ozone at STP were passed through 100 mL of 10 volume H_2O_2 solution. What is the volume strength of H_2O_2 after the reaction?
(1) 9.5 (2) 9.0 (3) 4.75 (4) 4.5
- 10 mL of a solution of H_2O_2 of 10 volume strength decolourises 100 mL of KMnO_4 solution acidified with dil H_2SO_4 . The amount of KMnO_4 in the given solution is ($K = 39$, $Mn = 55$)
(1) 0.282 g (2) 0.564 g (3) 1.128 g (4) 0.155 g
- 25 mL samples of distilled water, tap water, and boiled water required, respectively, 1 mL, 13 mL and 5 mL of soap solution to form a permanent lather. The ratio of temporary to permanent hardness in the tap water is
(1) 3:2 (2) 2:3 (3) 1:2 (4) 2:1
- 3.4 g sample of H_2O_2 solution containing $x\%$ H_2O_2 by weight requires x mL of a KMnO_4 solution for complete oxidation under acidic condition. The normality of KMnO_4 solution is
(1) 1 N (2) 2 N (3) 3 N (4) 0.5 N
- If 100 mL of acidified 2 N H_2O_2 is allowed to react with KMnO_4 solution till there is a light tinge of purple colour, the volume of oxygen produced at STP is
(1) 2.24 L (2) 1.12 L (3) 3.36 L (4) 4.48 L
- In the following equation:
$$\text{CrO}_4^{2-} + \text{S}_2\text{O}_3^{2-} + \text{OH}^- \longrightarrow [\text{Cr}(\text{OH})_4]^{-1} + \text{SO}_4^{2-}$$

What volume of 0.2 M Na_2CrO_4 solution is required just to react with 30 mL of 0.2 M $\text{Na}_2\text{S}_2\text{O}_3$ solution.
(1) 40 mL (2) 80 mL (3) 20 mL (4) 60 mL
- A balloon blown up has a volume of 300 mL at 27°C . The balloon is distended to $5/6$ of its maximum stretching capacity. The maximum temperature above which it will burst is
(1) 77°C (2) 67°C (3) 57°C (4) 87°C
- How many moles of MnO_4^- ion will react with 1 mol of ferrous oxalate in acidic medium?
(1) $\frac{1}{5}$ (2) $\frac{2}{5}$ (3) $\frac{3}{5}$ (4) $\frac{5}{3}$
- In a reaction, 4 mol of electrons are transferred to 1 mol of HNO_3 . The possible product obtained due to reduction is
(1) 0.5 mol of N_2 (2) 0.5 mol of N_2O
(3) 1 mol of NO_2 (4) 1 mol of NH_3
- If equal volumes of 1 M KMnO_4 and 1 M $\text{K}_2\text{Cr}_2\text{O}_7$ solutions are allowed to oxidise Fe (II) to Fe (III) in acidic medium, then Fe (II) oxidised will be
(1) More by KMnO_4 (2) More by $\text{K}_2\text{Cr}_2\text{O}_7$
(3) Equal in both cases (4) Can't be determined
- Sulphuryl chloride SO_2Cl_2 reacts with water to give a mixture of H_2SO_4 and HCl. Moles of NaOH required to

neutralise the solution formed by adding 1 mol of SO_2Cl_2 to excess water is are

- (1) 1 (2) 2 (3) 3 (4) 4

23. 100 mL of 0.01 M KMnO_4 oxidised 100 mL H_2O_2 in acidic medium. Volume of the same KMnO_4 required in alkaline medium to oxidise 100 mL of the same H_2O_2 will be (MnO_4^- changes to Mn^{2+} in acidic medium and to MnO_2 in alkaline medium)

- (1) $\frac{100}{3}$ mL (2) $\frac{500}{3}$ mL (3) $\frac{300}{5}$ mL (4) None of these

24. 10 mL of H_2O_2 solution (volume strength = x) required 10 mL of $\text{N}/0.56 \text{ MnO}_4^-$ solution in acidic medium. Hence, x is:

- (1) 0.56 (2) 5.6 (3) 0.1 (4) 10

25. $4\text{I}^- + \text{Hg}^{2+} \longrightarrow \text{HgI}_4^{2-}$

1 mol each of Hg^{2+} and I^- will form HgI_4^{2-}

- (1) 1 mol (2) 0.5 mol (3) 0.25 mol (4) 2 mol

26. In the mixture of ($\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$), volume of HCl required is x mL with phenolphthalein indicator and then y mL with methyl orange indicator in same titration. Hence, volume of HCl for complete reaction of Na_2CO_3 is:

- (1) $2x$ (2) y (3) $\frac{x}{2}$ (4) $(y - x)$

27. Equivalent weight of MnO_4^- in acidic, neutral and basic media are in ratio of:

- (1) 3:5:15 (2) 5:3:1 (3) 5:1:13 (4) 3:15:5

28. $\text{NH}_3 + \text{OCl}^- \longrightarrow \text{N}_2\text{H}_4 + \text{Cl}^-$

On balancing the above equation in basic solution, using integral coefficient, which of the following whole numbers will be the coefficient of N_2H_4 ?

- (1) 1 (2) 2 (3) 3 (4) 4

29. In an experiment, 50 mL of 0.1 M solution of a metallic salt reacted exactly with 25 mL of 0.1 M solution of sodium sulphite. In the reaction, SO_3^{2-} is oxidised to SO_4^{2-} . If the original oxidation number of the metal in the salt was 3, what would be the new oxidation number of the metal?

- (1) 0 (2) 1 (3) 2 (4) 4

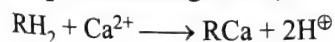
30. 20 mL of x M HCl neutralises completely 10 mL of 0.1 M NaHCO_3 solution and a further 5 mL of 0.2 M Na_2CO_3 solution to methyl orange end point. The value of x is

- (1) 0.167 M (2) 0.133 M (3) 0.15 M (4) 0.2 M

31. The normality and volume strength of a solution made by mixing 1.0 L each of 5.6 vol and 11.2 vol H_2O_2 solution are

- (1) 1 N, 5.6 vol (2) 1.5 N, 5.6 vol
(3) 1.5 N, 8.4 vol (4) 1 N, 8.4 vol

32. RH_2 (ion exchange resin) can replace Ca^{2+} in hard water



1 L of hard water after passing through RH_2 has $\text{pH} = 2$. Hence, hardness in ppm of Ca^{2+} is

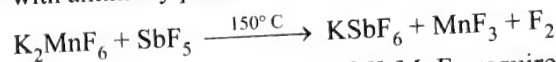
- (1) 200 (2) 100 (3) 50 (4) 125

33. 100 mL of H_2O_2 is oxidised by 100 mL of 0.01 M KMnO_4 in acidic medium (MnO_4^- reduced to Mn^{2+}). 100 mL of the

same H_2O_2 is oxidised by V mL of 0.01 M KMnO_4 in basic medium (MnO_4^- reduced to MnO_2). Hence, V is

- (1) 500 (2) 100 (3) $\frac{100}{3}$ (4) $\frac{500}{3}$

34. F_2 can be prepared by reacting hexafluoro manganate (IV) with antimony pentafluoride as:



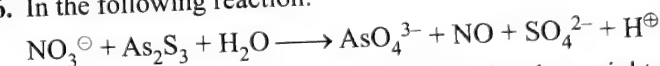
The number of equivalent of K_2MnF_6 required to react completely with one mol of SbF_5 in the given reaction is.

- (1) 1.52 (2) 5.0 (3) 0.5 (4) 4.0

35. 3 mol of a mixture of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ required 100 mL of 2 M KMnO_4 solution in acidic medium. Hence, mole fraction of FeSO_4 in the mixture is

- (1) $\frac{1}{3}$ (2) $\frac{2}{3}$ (3) $\frac{2}{5}$ (4) $\frac{3}{5}$

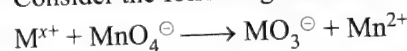
36. In the following reaction:



the equivalent weight of As_2S_3 (with molecular weight M) is:

- (1) $\frac{3M}{28}$ (2) $\frac{M}{4}$ (3) $\frac{M}{24}$ (4) $\frac{M}{28}$

37. Consider the following reaction:



If 1 mol of MnO_4^- oxidises 1.67 mol of M^{x+} to MO_3^- , then the value of x in the reaction is

- (1) 2 (2) 3 (3) 4 (4) 5

38. In the mixture of NaHCO_3 and Na_2CO_3 , the volume of a given HCl required is x mL with phenolphthalein indicator and further y mL required with methyl orange indicator. Hence, volume of HCl for complete reaction of NaHCO_3 is

- (1) $2x$ (2) y (3) $\frac{x}{2}$ (4) $(y - x)$

39. 10 mL of NaHC_2O_4 is oxidised by 10 mL of 0.02 M MnO_4^- . Hence, 10 mL of NaHC_2O_4 is neutralised by

- (1) 10 mL of 0.1 M NaOH (2) 10 mL of 0.02 M NaOH
(3) 10 mL of 0.1 M $\text{Ca}(\text{OH})_2$ (4) 10 mL of 0.05 N $\text{Ba}(\text{OH})_2$

40. 1 mol of ferric oxalate is oxidised by x mol of MnO_4^- in acidic medium. Hence, the value of x is

- (1) 1.2 (2) 1.6 (3) 1.8 (4) 1.5

41. 40 mL of 0.05 M solution of sodium sesquicarbonate ($\text{Na}_2\text{CO}_3\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is titrated against 0.05 M HCl. x mL of HCl is used when phenolphthalein is the indicator and y mL of HCl is used when methyl orange is the indicator in two separate titrations. Hence $(y - x)$ is

- (1) 80 mL (2) 30 mL (3) 120 mL (4) None

42. What volume of 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium is needed for complete oxidation of 200 mL of 0.6 M FeC_2O_4 solution?

- (1) 1.2 mL (2) 1.2 L (3) 120 mL (4) 800 mL

43. 1 mol of MnO_4^{2-} in neutral aqueous medium disproportionates to

- (1) $\frac{2}{3}$ mol of MnO_4^- and $\frac{1}{3}$ mol of MnO_2
 (2) $\frac{1}{3}$ mol of MnO_4^- and $\frac{2}{3}$ mol of MnO_2
 (3) $\frac{1}{3}$ mol of Mn_2O_7 and $\frac{2}{3}$ mol of MnO_2
 (4) $\frac{2}{3}$ mol of Mn_2O_7 and $\frac{1}{3}$ mol of MnO_2
44. If equal volumes of 1 M KMnO_4 and 1 M $\text{K}_2\text{Cr}_2\text{O}_7$ solutions are used to oxidise Fe^{2+} in acidic medium, then Fe^{2+} will be oxidised
 (1) More by $\text{K}_2\text{Cr}_2\text{O}_7$
 (2) More by KMnO_4
 (3) Equal in both the cases
 (4) The data is insufficient to predict the answer
45. The volume strength of 1.5 N H_2O_2 solution is
 (1) 4.8 (2) 8.4 (3) 3.0 (4) 8.0
46. The equivalent weight of MnSO_4 is half its molecular weight when it is converted to
 (1) Mn_2O_3 (2) MnO_2 (3) MnO_4^- (4) MnO_4^{2-}
47. What volume of 0.2 M KMnO_4 is required to react with 1.58 g of hypo solution ($\text{Na}_2\text{S}_2\text{O}_3$) in acidic medium?
 (1) 20 mL (2) 10 mL (3) 16.6 mL (4) 50 mL
48. In basic medium, CrO_4^{2-} reacts with $\text{S}_2\text{O}_3^{2-}$ resulting in the formation of $\text{Cr}(\text{OH})_4^-$ and SO_4^{2-} . How many mL of 0.1 M Na_2CrO_4 is required to react with 40 mL of 0.25 M $\text{Na}_2\text{S}_2\text{O}_3$?
 (1) 240.2 mL (2) 24.02 mL (3) 266.67 mL (4) 26.67 mL
49. A 0.46 g sample of As_2O_3 required 25.0 mL of KMnO_4 solution for its titration. The molarity of KMnO_4 solution is
 (1) 0.016 (2) 0.074 (3) 0.032 (4) 0.128
50. Number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ reduced by 1 mol of Sn^{2+} is
 (1) $\frac{1}{3}$ (2) $\frac{1}{6}$ (3) $\frac{2}{3}$ (4) 1
51. 10 mL of H_2O_2 solution (volume strength = x) required 10 mL of N/0.56 MnO_4^- solution in acidic medium. Hence, x is
 (1) 0.56 (2) 5.6 (3) 0.1 (4) 10
52. Equivalent weight of H_3PO_2 (molecular weight = M) when it disproportionates into PH_3 and H_3PO_3 is
 (1) M (2) $\frac{M}{2}$ (3) $\frac{M}{4}$ (4) $\frac{3M}{4}$
53. The volume of 0.5 M H_3PO_4 that completely dissolves 3.1 g of copper carbonate is (molecular mass of copper carbonate = 124 g mol^{-1})
 (1) 55.5 mL (2) 45.5 mL (3) 35.5 mL (4) 33.3 mL
54. 0.4 g of polybasic acid HnA (all the hydrogens are acidic) requires 0.5 g of NaOH for complete neutralisation. The number of replaceable hydrogen atoms and the molecular weight of 'A' would be (M_w of acid = 96)
 (1) 2, 94 (2) 1, 95 (3) 3, 93 (4) 4, 92
55. A mixed solution of potassium hydroxide and sodium carbonate required 15 mL of an N/20 HCl solution when titrated with phenolphthalein as an indicator. But the same amount of the solution when titrated with methyl orange as indicator required 25 mL of the same acid. The amount of KOH present in the solution is
 (1) 0.014 g (2) 0.14 g (3) 0.028 g (4) 1.4 g
56. 25.0 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in water containing dilute H_2SO_4 , and the volume was made up to 1.0 L. 25.0 mL of this solution required 20 mL of an N/10 KMnO_4 solution for complete oxidation. The percentage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the acid solution is
 (1) 78% (2) 98% (3) 89% (4) 79%
57. A 0.13 g of a specimen containing MnO_2 is treated with iodide ions. If iodine liberated requires 30.0 mL of 0.075 M solution of $\text{Na}_2\text{S}_2\text{O}_3$, the percentage of MnO_2 in the mineral is
 (1) 75.3% (2) 85.3% (3) 95.3% (4) None
58. The mass of $\text{K}_2\text{Cr}_2\text{O}_7$ required to produce 5.0 L CO_2 at 77°C and 0.82 atm pressure from excess of oxalic acid and volume of 0.1 N NaOH required to neutralise the CO_2 evolved, respectively, are
 (1) 7 g, 2.86 L (2) 5 g, 1.86 L
 (3) 4 g, 0.86 L (4) None
59. A mixture of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ required equal volumes of 0.2 M KMnO_4 and 0.2 M NaOH separately for complete titration. The mole ratio of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ in the mixture is
 (1) $\frac{2}{11}$ (2) $\frac{11}{2}$ (3) $\frac{5}{2}$ (4) $\frac{7}{2}$
60. The weight of MnO_2 and the volume of HCl of specific gravity 1.2 g mL^{-1} and 4% nature by weight, needed to produce 1.78 L of Cl_2 at STP. The reaction involved is:
 $\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$
 (1) 0.48 L (2) 0.24 L (3) 0.12 L (4) 0.06 L
61. In the reaction
 $\text{CrO}_5 + \text{H}_2\text{SO}_4 \longrightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{O}_2$
 1 mol of CrO_5 will liberate how many moles of O_2 ?
 (1) $\frac{5}{2}$ (2) $\frac{5}{4}$
 (3) $\frac{9}{2}$ (4) None of these
62. The purity of H_2O_2 in a given sample is 85%. Calculate the weight of impure sample of H_2O_2 which requires 10 mL of M/5 KMnO_4 solution in a titration in acidic medium.
 (1) 2 g (2) 0.2 g (3) 0.17 (4) 0.15 g
63. 0.848 g aqueous solution of a mixture containing Na_2CO_3 , NaOH , and an inert matter is titrated with M/2 HCl . The colour of phenolphthalein disappears when 20 mL of the acid has been added. Methyl orange is then added and 8.0

mL more of the acid is required to give a red colour to the solution. The percentage of Na_2CO_3 is

- (1) 25 (2) 12.5 (3) 75 (4) 50

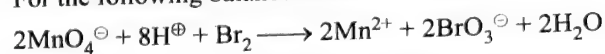
Multiple Correct Answers Type

- What volume of 0.1 M KMnO_4 in acidic medium is required for complete oxidation of 100 mL of 0.1 M FeC_2O_4 and 100 mL of 0.1 M ferric oxalate separately.
 - 60 mL of KMnO_4 with FeC_2O_4
 - 40 mL of KMnO_4 with FeC_2O_4
 - 40 mL of KMnO_4 with ferric oxalate
 - 120 mL of KMnO_4 with ferric oxalate
- Which of the following statements about the following reaction is/are not correct?

$$\text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{O}_2$$
 - H_2O_2 is oxidised to O_2 .
 - H_2O_2 is reduced to H_2O .
 - The oxidation number of chromium atom changes by 3.
 - Hydrogen ions are oxidised to H_2O .
- 0.1 mol of MnO_4^- (in acidic medium) can:
 - Oxidise 0.5 mol of Fe^{2+}
 - Oxidise 0.166 mol of FeC_2O_4
 - Oxidise 0.25 mol of $\text{C}_2\text{O}_4^{2-}$
 - Oxidise 0.6 mol of $\text{Cr}_2\text{O}_7^{2-}$
- $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 behave as acids as well as reducing agents. Which of the following are correct statements?
 - Equivalent weights of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 are equal to their molecular weights when acting as reducing agents.
 - Equivalent weights of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 are equal to half their molecular weights when acting as reducing agents.
 - 100 mL of 1 M solution of each is neutralised by equal volumes of 1 N $\text{Ca}(\text{OH})_2$
 - 100 mL of 1 M solution of each is oxidised by equal volumes of 1 M KMnO_4 .
- A compound contains atoms of three elements A, B, and C. If the oxidation number of A is +2, B is +5, and C is -2, the possible formula of the compound is:
 - $\text{A}(\text{BC}_3)_2$
 - $\text{A}_3(\text{BC}_4)_2$
 - $\text{A}_3(\text{B}_4\text{C})_2$
 - ABC_2
- Choose the correct statement:
 - 1 mol of MnO_4^- ion can oxidise 5 mol of Fe^{2+} ion in acidic medium.
 - 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ ion can oxidise 6 mol of Fe^{2+} ion in acidic medium.

- 1 mol of Cu_2S can be oxidised by 1.6 mole of MnO_4^- ion in acidic medium.
- 1 mol of CuS can be oxidised by 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ ion in acidic medium.

7. For the following balanced redox reaction:



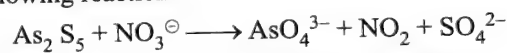
if the molecular weight of MnO_4^- , Br_2 and Br_2 be M_1 , M_2 respectively, then

- Equivalent weight of MnO_4^- is $M_1/5$
- Equivalent weight of Br_2 is $M_2/10$
- The n -factor ratio of MnO_4^- : Br_2 is 1 : 1
- None of these

8. Which of the following statements is/are correct about 6.8% strength of H_2O_2 ?

- Its normality is 4 N.
- Its molarity is 2 M.
- Its volume strength is 22.4 V.
- Volume strength = $11.2 \times \text{M}$.

9. Which of the following statements is/are correct in the following reaction.



- The equivalent weight of As_2S_5 is $M/40$. (M = molecular weight of As_2S_5).
- The equivalent weight of NO_3^- is $M/3$. (M = molecular weight of NO_3^- ion)
- n -factor for the conversion of As_2S_5 to AsO_4^{3-} is zero.
- n -factor for the conversion of As_2S_5 to SO_4^{2-} is 30.

10. x g of H_2O_2 requires 100 mL of $M/5$ KMnO_4 in a titration in a solution having $\text{pOH} = 1.0$

Which of following is/are correct?

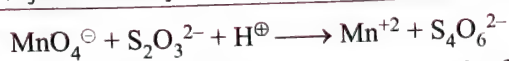
- The value of x is 1.7 g.
- The value of x is 0.34 g.
- MnO_4^- changes to MnO_4^{2-}
- H_2O_2 changes to O_2 .

11. A mixture of n_1 moles of $\text{Na}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 is titrated separately with H_2O_2 and KOH , to reach at equivalence point.

Which of the following statements is/are correct?

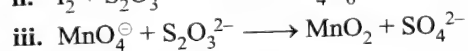
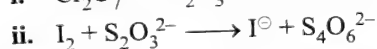
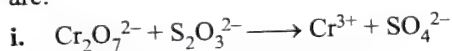
- Moles of H_2O_2 and KOH are $n_1 + n_2$ and n_2 .
- Moles of H_2O_2 and KOH is: $n_1 + \frac{n_2}{2}$ and n_1 .
- n -factors of NaHC_2O_4 with KOH and H_2O_2 , respectively, are 1 and 2.
- n -factors of $\text{Na}_2\text{C}_2\text{O}_4$ with H_2O_2 and KOH , respectively, are 2 and 1.

12. Which of the following is/are correct about the redox reaction?



- (1) 1 mol of $\text{S}_2\text{O}_3^{2-}$ is oxidised by 8 mol. of MnO_4^-
- (2) The above redox reaction with the change of pH from 4 to 10 will have an effect on the stoichiometry of the reaction.
- (3) Change of pH from 4 to 7 will change the nature of the product.
- (4) At pH = 7, $\text{S}_2\text{O}_3^{2-}$ ions are oxidised to HSO_4^-
13. 20 mL of H_2O_2 is reacted completely with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution. 40 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution was required to oxidise the H_2O_2 completely. Also, 2.0 mL of the same $\text{K}_2\text{Cr}_2\text{O}_7$ solution required 5.0 mL of a 1.0 M $\text{H}_2\text{C}_2\text{O}_4$ solution to reach equivalence point.
- Which of the following statements is/are correct?
- (1) The H_2O_2 solution is 5 M.
- (2) The volume strength of H_2O_2 is 56 V.
- (3) The volume strength of H_2O_2 is 112 V.
- (4) If 40 mL of 5 M/8 H_2O_2 is further added to the 10 mL of above H_2O_2 solution the volume strength of the resulting solution is changed to 16.8 V.

14. Three different solutions of oxidising agents, $\text{K}_2\text{Cr}_2\text{O}_7$, I_2 , and KMnO_4 is titrated separately with 0.19 g of $\text{K}_2\text{S}_2\text{O}_3$. The molarity of each oxidising agent is 0.1 M and the reactions are:



(Molecular weight of $\text{K}_2\text{S}_2\text{O}_3 = 190$, $\text{K}_2\text{Cr}_2\text{O}_7 = 294$, $\text{KMnO}_4 = 158$, and $\text{I}_2 = 254 \text{ g mol}^{-1}$)

Which of the following statements is/are correct?

- (1) All three oxidising agents can act as self-indicators.
- (2) Volume of I_2 used is minimum.
- (3) Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used is maximum.
- (4) Weight of KMnO_4 used in the titration is maximum.
15. The hardness of water due to HCO_3^- is 122 ppm. Select the correct statement(s).
- (1) The hardness of water in terms of CaCO_3 is 200 ppm.
- (2) The hardness of water in terms of CaCO_3 is 100 ppm.
- (3) The hardness of water in terms of CaCl_2 is 222 ppm.
- (4) The hardness of water in terms of MgCl_2 is 95 ppm.

Linked Comprehension Type

Paragraph 1

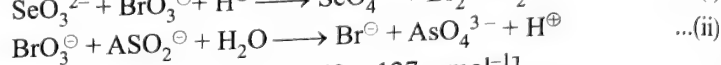
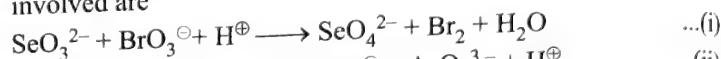
KMnO_4 reacts with $\text{Na}_2\text{S}_2\text{O}_3$ is acidic, strongly basic, and aqueous (neutral) media. 100 mL of KMnO_4 reacts with 100 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ in acidic, basic, and neutral media.

1. The molarity (M) of KMnO_4 solution in the acidic medium is
- (1) 0.2 M (2) 0.02 M (3) 0.4 M (4) 0.04 M

2. The molarity (M) of KMnO_4 solution in basic medium is:
- (1) 0.8 M (2) 0.08 M (3) 0.26 M (4) 0.026 M
3. The molarity (M) of KMnO_4 in aqueous medium is:
- (1) 0.8 M (2) 0.08 M (3) 0.26 M (4) 0.026 M
4. The molality (m) of KMnO_4 in the acidic medium is: (Density of KMnO_4 solution = 1.58 g mL^{-1} $M_w(\text{KMnO}_4) = 158 \text{ g mol}^{-1}$)
- (1) 0.025 (2) 0.25 (3) 0.12 (4) 0.012

Paragraph 2

20 mL of M/60 KBrO_3 was reacted with a sample of SeO_3^{2-} . The Br_2 thus evolved was removed and the excess of KBrO_3 was titrated with 5 mL of M/60 solution of NaAsO_2 . The reactions involved are



$$[M_w(\text{SeO}_3^{2-}) = 79 + 48 = 127 \text{ g mol}^{-1}]$$

5. n -factors of BrO_3^- ion in equations (i) and (ii), respectively, are
- (1) 10, 6 (2) 5, 6 (3) 6, 10 (4) 6, 5
6. Excess mEq of BrO_3^- in reaction (ii) is
- (1) $\frac{1}{6}$ (2) $\frac{11}{6}$ (3) $\frac{1}{36}$ (4) $\frac{11}{36}$
7. mEq of SeO_3^{2-} is
- (1) $\frac{55}{72}$ (2) $\frac{55}{36}$ (3) $\frac{11}{36}$ (4) $\frac{11}{6}$
8. Amount of SeO_3^{2-} in mg is
- (1) 19.4 mg (2) 194 mg (3) 970 mg (4) 97 mg
9. Which of the following is true (T) or false (F)?
- (1) Excess of mEq of $\text{BrO}_3^- = \text{mEq of AsO}_2^-$ in reaction (ii).
- (2) mEq of $\text{SeO}_3^{2-} = \text{Total mEq of BrO}_3^-$
- (3) mmol of $\text{SeO}_3^{2-} = \text{Total mmol of BrO}_3^- - \text{mmol of BrO}_3^- (\text{excess})$ in reaction (ii)
- (4) mEq of $\text{SeO}_3^{2-} = \text{Total mEq of BrO}_3^- - \text{mEq of BrO}_3^- (\text{excess})$ used in reaction (ii)

Paragraph 3

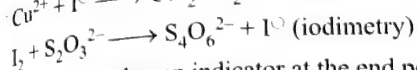
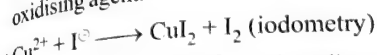
If 20 mL M/10 $\text{Ba}(\text{MnO}_4)_2$ completely reacts with FeC_2O_4 in acidic medium,

10. mEq of FeC_2O_4 reacted is
- (1) 6 (2) 20 (3) 40 (4) None
11. Millimoles of FeC_2O_4 reacted is
- (1) $\frac{20}{3}$ (2) $\frac{20}{2}$ (3) $\frac{20}{6}$ (4) $\frac{20}{10}$
12. What is the volume of CO_2 produced at STP.
- (1) 112 mL (2) 224 mL (3) 448 mL (4) None

Paragraph 4

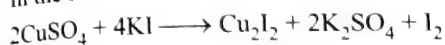
Direct titration of I_2 with a reducing agent is called iodimetry. If I_2 is liberated by the oxidation of I^- ion by a strong oxidising agent in neutral or acidic medium, the liberated I_2 is then titrated with a

reducing agent. Iodometry is used to estimate the strength of the oxidising agent. For example, in the estimation of Cu^{2+} with $\text{S}_2\text{O}_3^{2-}$.



Starch is used as an indicator at the end point, which forms blue-coloured complex with I_3^- . Disappearance of blue colour indicates the end point when free I_2 is not present.

13. In the reaction



The equivalent weight of CuSO_4 is

(Mw = 159.5 g mol⁻¹)

- (1) Mw (2) $\frac{\text{Mw}}{2}$ (3) $\frac{\text{Mw}}{4}$ (4) $\frac{\text{Mw}}{8}$

14. 638.0 g of CuSO_4 solution is titrated with excess of 0.2 M KI solution. The liberated I_2 required 400 mL of 1.0 M $\text{Na}_2\text{S}_2\text{O}_3$ for complete reaction. The percentage purity of CuSO_4 in the sample is

- (1) 5% (2) 10% (3) 15% (4) 20%

15. The volume of KI solution used for CuSO_4 is:

- (1) 1 L (2) 2 L (3) 4 L (4) 5 L

Paragraph 5

In the study of titration of NaOH and Na_2CO_3 , NaOH and NaHCO_3 , Na_2CO_3 and NaHCO_3 , phenolphthalein and methyl orange are used as indicators.

(a) When phenolphthalein is used as an indicator for the above mixture:

- It indicates complete neutralisation of NaOH or KOH
- It indicates half neutralisation of Na_2CO_3 because NaHCO_3 is formed at the end point

(b) When methyl orange is used as an indicator for the above mixture

- It indicates complete neutralisation of NaOH or KOH
- It indicates half neutralisation of Na_2CO_3 because NaCl is formed at the end point

16. A 10 g mixture of NaHCO_3 and KOH is dissolved in water to make 1000 mL solution. 100 mL of this solution required 50 mL of 0.2 M HCl for complete neutralisation in the presence of phenolphthalein as indicator. What is the percentage of NaHCO_3 in the mixture?

- (1) 50% (2) 56% (3) 44% (4) 60%

17. 1 L solution of Na_2CO_3 and NaOH was made in H_2O . 100 mL of this solution required 20 mL of 0.4 M HCl in the presence of phenolphthalein. However, another 100 mL sample of the same solution required 25 mL of the same acid in the presence of methyl orange as indicator. What is the molar ratio of Na_2CO_3 and NaOH in the original mixture

- (1) 3:2 (2) 3:1 (3) 1:3 (4) 1:1

18. In Q. (24), what is the strength of NaOH in the original solution.

- (1) 4 g L⁻¹ (2) 2.4 g L⁻¹ (3) 4.8 g L⁻¹ (4) 6 g L⁻¹

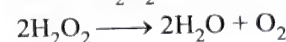
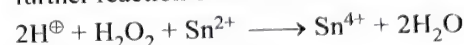
19. In Q. 24, what is the strength of Na_2CO_3 in the original solution?

- (1) 2.12 g L⁻¹ (2) 1.06 g L⁻¹ (3) 3.18 g L⁻¹ (4) 4.24 g L⁻¹

Paragraph 6

H_2O_2 is reduced rapidly by Sn^{2+} to give H_2O and Sn^{4+} . H_2O_2 is decomposed slowly at room temperature to yield O_2 and H_2O .

136 g of 10% by mass of H_2O_2 in water is treated with 100 mL of 3 M Sn^{2+} and then the mixture is allowed to stand until no further reaction occurs. The reaction involved are:



20. The Eq of H_2O_2 reacted with Sn^{2+} is

- (1) 0.2 (2) 0.3 (3) 0.4 (4) 0.6

21. The Eq of H_2O_2 left after reacting with Sn^{2+} is:

- (1) 0.1 (2) 0.2 (3) 0.3 (4) 0.4

22. The volume strength of H_2O_2 left after reacting with Sn^{2+} is

- (1) 1.12 V (2) 11.2 V (3) 2.24 V (4) 22.4 V

23. Calculate the volume of O_2 produced at 27°C and 1.0 atm after H_2O_2 is reacted with Sn^{2+} and the mixture is allowed to stand.

- (1) 2.46 L (2) 4.92 L (3) 1.23 L (4) 7.38 L

Paragraph 7

Three solutions, each of 100 mL, containing 0.4 M As_2S_3 , 5 M NaOH and 6 M H_2O_2 , respectively, were mixed to form AsO_4^{3-} and SO_4^{2-} as products.

24. Which of the following options is correct about the coefficients of reactants and products in a balanced equation?

	As_2S_3	OH^-	H_2O_2	AsO_4^{3-}	SO_4^{2-}	H_2O
(1)	1	12	12	2	3	20
(2)	1	12	14	2	3	20
(3)	2	12	12	1	2	16
(4)	2	14	14	1	2	16

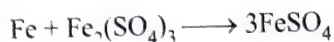
25. Which of the following options is correct about the molarities of each species left at the end of the reaction?

	NaOH	H_2O_2	AsO_4^{3-}	SO_4^{2-}	H_2O
(1)	$\frac{\text{M}}{15}$	$\frac{2\text{M}}{15}$	$\frac{4\text{M}}{15}$	$\frac{6\text{M}}{15}$	$\frac{8\text{M}}{3}$
(2)	$\frac{\text{M}}{15}$	$\frac{2\text{M}}{15}$	$\frac{4\text{M}}{15}$	$\frac{6\text{M}}{15}$	$\frac{4\text{M}}{3}$
(3)	$\frac{\text{M}}{15}$	$\frac{2\text{M}}{15}$	$\frac{4\text{M}}{15}$	$\frac{6\text{M}}{15}$	$\frac{\text{M}}{3}$
(4)	$\frac{\text{M}}{15}$	$\frac{2\text{M}}{15}$	$\frac{4\text{M}}{15}$	$\frac{6\text{M}}{15}$	$\frac{\text{M}}{15}$

26. When the above solution is allowed to stand for some time, what volume of O_2 will be obtained at STP?
 (1) 0.112 L (2) 0.224 L (3) 0.448 L (4) 0.336 L
27. Percentage strength of the H_2O_2 solution left after reaction is
 (1) 0.017% (2) 0.113% (3) 0.51% (4) 0.68%

Paragraph 8

100 mL solution of ferric alum $[Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O]$ ($M_v = 964 \text{ g mol}^{-1}$) containing 2.41 g of salt was boiled with Fe when the reaction



takes place. The unreacted iron was filtered off and the solutions was titrated with $M/60 \text{ K}_2\text{Cr}_2\text{O}_7$ in acidic medium.

28. Moles of $FeSO_4$ formed when Fe reacts with $Fe_2(SO_4)_3$ is
 (1) 0.0075 (2) 0.005 (3) 0.001 (4) 0.002
29. Moles of $FeSO_4$ formed when Cu reacts with $Fe_2(SO_4)_3$ is
 (1) 0.0075 (2) 0.005 (3) 0.001 (4) 0.002
30. What is the titre value of $K_2Cr_2O_7$ when Fe reacts with $Fe_2(SO_4)_3$?
 (1) 25 mL (2) 50 mL (3) 75 mL (4) 100 mL
31. What is the titre value of $K_2Cr_2O_7$ when Cu reacts with $Fe_2(SO_4)_3$?
 (1) 25 mL (2) 50 mL (3) 75 mL (4) 100 mL

Paragraph 9

10 mL solution of H_2SO_4 and $H_2C_2O_4$ (oxalic acid), on titration with 0.1 M KOH, required 20 mL of the base. 10 mL of the same solution on titration with $M/300 \text{ K}_2\text{Cr}_2\text{O}_7$ required 50 mL of $K_2Cr_2O_7$.

32. Strength of oxalic acid in the solution is:
 (1) 4.5 g L^{-1} (2) 4.9 g L^{-1} (3) 2.25 g L^{-1} (4) 2.45 g L^{-1}
33. The strength of H_2SO_4 in the solution is
 (1) 4.5 g L^{-1} (2) 4.9 g L^{-1} (3) 2.25 g L^{-1} (4) 2.45 g L^{-1}
34. What should be the volume strength of H_2O_2 , if H_2O_2 reacts with the same volume of $M/300 \text{ K}_2\text{Cr}_2\text{O}_7$ solution.
 (1) 5.6 V (2) 0.56 V (3) 11.2 V (4) 1.12 V

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1.	Column I		Column II
	Redox reaction		Value of x
a.	1 mol of MnO_4^{2-} can oxidise x mol of Fe^{2+} ions in acidic medium.	p.	6
b.	1 mol of CuS can be oxidised by x mol of $Cr_2O_7^{2-}$ ion in acidic medium.	q.	5

c.	1 mol of Cu_2S can be oxidised by x mol of MnO_4^{2-} ion in acidic medium.	r.	1
d.	1 mol of $Cr_2O_7^{2-}$ ion oxidise x mol of Fe^{2+} ion in acidic medium.	s.	1.6

2. Given two mixtures: (A) NaOH and Na_2CO_3 (B) and $NaHCO_3$ and Na_2CO_3 .

100 mL of mixture (A) required a and b mL of 1M HCl in separate titration using phenolphthalein and methyl orange indicators while 100 mL of mixture (B) required x and y mL of same HCl solution in separate titration using the same indicators.

	Column I		Column II
	Mixture component		Milli moles
a.	Na_2CO_3 in mixture (A)	p.	$(2a - b)$
b.	Na_2CO_3 in mixture (B)	q.	$(y - 2x)$
c.	NaOH in mixture (A)	r.	x
d.	$NaHCO_3$ in mixture (B)	s.	$(b - a)$

3.

S.No.	Column I Reaction		Column II Characteristics
a.	For the balanced redox reaction:	p.	$E_w(Br_2) = \frac{3M}{5}$
	$2MnO_4^- + 8H^+ + Br_2 \rightarrow 2Mn^{2+} + 2BrO_3^- + 2H_2O$		
b.	$Br_2 + OH^- \rightarrow Br^- + BrO_3^-$	q.	$E_w(Br_2) = \frac{M}{10}$
c.	$H_2C_2O_4$ and $NaHC_2O_4$ behaves as acid	r.	Equivalent weights of $H_2C_2O_4$ and $NaHC_2O_4$ are equal to half their molecular weights.
d.	$H_2C_2O_4$ and $NaHC_2O_4$	s.	$E_w(H_2C_2O_4) = \frac{M}{2}$ as reducing agents $E_w(NaHC_2O_4) = M$

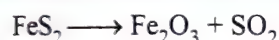
4.

S.No.	Column I Reaction		Column II The value of x
a.	5 mol of an equimolar mixture of ferric oxalate and ferrous oxalate will require x mol of $KMnO_4$ in acidic medium for complete oxidation.	p.	11.0

b.	5 mol of an equimolar mixture of ferric oxalate and ferrus oxalate will require x mol of $K_2Cr_2O_7$ in acidic medium for complete oxidation.	q.	7.0
c.	5 mol of an equimolar mixture of CuS and Cu_2S will require x mol of $KMnO_4$ in acidic medium for complete oxidation.	r.	4.5
d.	12 mol of an equimolar mixture of CuS and Cu_2S will require x mol of $K_2Cr_2O_7$ in acidic medium for complete oxidation.	s.	3.75
e.	4 mol of an equimolar mixture of $KMnO_4$ and $K_2Cr_2O_7$ will require x mol of H_2O_2 in acidic medium for complete reduction.	t.	14.0

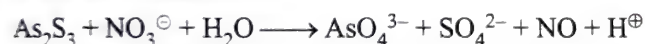
Numerical Value Type

1. n -factors for the following reaction is



(1) 8 (2) 9 (3) 10 (4) 11

2. In the following reaction



The number of electrons involved in the oxidation reaction is

(1) 22 (2) 24 (3) 26 (4) 28

3. In Q. 2 the number of electrons involved in the reduction reaction is

(1) 4 (2) 3 (3) 2 (4) 1

4. n -factors of ferrous oxalate and ferric oxalate when they react with $K_2Cr_2O_7$ in acidic medium are

(1) 2, 6 (2) 6, 2 (3) 3, 6 (4) 6, 3

5. n -factors for Cu_2S and CuS when they react with $KMnO_4$ in acidic medium are

(1) 7, 7 (2) 6, 6 (3) 6, 8 (4) 8, 6

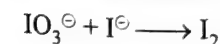
6. How many moles of H_2SO_4 are required to produce 1 mol of H_2S when KI reacts with H_2SO_4 producing I_2 and H_2S ?

(1) 5 (2) 4 (3) 3 (4) 2

7. The molarity of H_2O_2 of the 11.2 V (volume strength) is

(1) 2 M (2) 1 M (3) 3 M (4) 4 M

8. 1 mol of IO_3^- ions is heated with excess of I^- ions in the presence of acidic conditions as per the following equation



How many moles of acidified hypo solution will be required to react completely with I_2 thus produced?

(1) 1 (2) 3 (3) 5 (4) 6

9. A bottle of H_2O_2 is labelled as 10 vol H_2O_2 . 112 mL of this solution of H_2O_2 is titrated against 0.04 M acidified solution of $KMnO_4$. The volume of $KMnO_4$ in litre is

(1) 1 L (2) 2 L (3) 3 L (4) 4 L

10. 1 L M/10 $Ba(MnO_4)_2$ in acidic medium can be oxidised completely with 1/6 L of x M ferric oxalate. The value of x is

(1) 1 M (2) 2 M (3) 3 M (4) 4 M

11. The oxidation state of oxygen of H_2O_2 in the final products when it reacts with ClO_3^- is

(1) 0 (2) 1 (3) -1 (4) -2

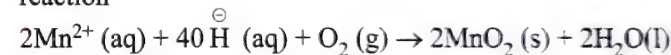
12. The oxidation state of oxygen of H_2O_2 in the final products when it reacts with As_2O_3 is

(1) 0 (2) 1 (3) -1 (4) -2

13. Washing soda ($Na_2CO_3 \cdot 10H_2O$) is widely used in softening of hard water. If 1 L of hard water requires 0.0286 g of washing soda, the hardness of $CaCO_3$ in ppm is

(1) 10 ppm (2) 5 ppm (3) 8 ppm (4) 6 ppm

14. Dissolved O_2 in water is determined by using a redox reaction



How many equivalents of O_2 will be required to react with 1 mol of Mn^{2+} ?

(1) 1 (2) 2 (3) 3 (4) 4

15. The normality of 2 M H_3BO_3 is

(1) 6 (2) 4 (3) 2 (4) 1

16. An acid solution of 0.2 mol of $KReO_4$ was reduced with Zn and then titrated with 1.6 Eq of acidic $KMnO_4$ solution. For the reoxidation of all the rhenium (Re) to the perrhenate ion (ReO_4^-). Assuming that rhenium was the only element reduced, what is the oxidate state to which rhenium was reduced by Zn?

(1) 1 (2) 2 (3) -1 (4) -2

17. A 200 mL solution of I_2 is divided into two unequal parts. Part I reacts with hypo solution in acidic medium and requires 8 mL of 2 M hypo solution for complete neutralisation.

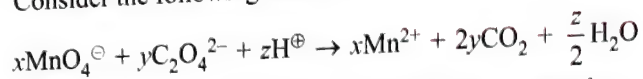
Part II was added with 300 mL of 0.1 M NaOH solution. Residual base required 30 mL of 0.1 M H_2SO_4 solution for complete neutralisation. Calculate the value of 20 times the initial concentration of I_2 ?

(1) 1 (2) 2 (3) 3 (4) 4

JEE ADVANCED

Single Correct Answer Type

1. Consider the following reaction:

The values of x , y and z in the reaction are, respectively:

- (1) 2, 5 and 8 (2) 2, 5 and 16
(3) 5, 2 and 8 (4) 5, 2 and 16

(JEE Advanced 2013)

Multiple Correct Answers Type

1. Reduction of the metal centre in aqueous permanganate ion involves

- (1) 3 electrons in neutral medium
(2) 5 electrons in neutral medium
(3) 3 electrons in alkaline medium
(4) 5 electrons in acidic medium

(IIT-JEE 2011)

Linked Comprehension Type

Bleaching powder and bleach solution are produced on a large scale and used in several house hold products. The effectiveness of bleach solution is often measured by iodometry.

1. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N
- $\text{Na}_2\text{S}_2\text{O}_3$
- was used to reach the end point. The molarity of the household bleach solution is

- (1) 0.48 M (2) 0.96 M
(3) 0.24 M (4) 0.024 M

2. Bleaching powder contains a salt of an oxoacid is one of its components. The anhydride of that oxoacid is

- (1) Cl_2O (2) Cl_2O_7
(3) ClO_2 (4) Cl_2O_4

(IIT-JEE 2012)

Numerical Value Type

1. The volume (in mL) of 0.1 M
- AgNO_3
- for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$
- , as silver chlorides is close to

(IIT-JEE 2011)

2. Reaction of
- Br_2
- with
- Na_2CO_3
- in aqueous solution gives sodium bromide and sodium bromate with evolution of
- CO_2
- gas. The number of sodium bromide molecules involved in the balanced chemical equation is

(IIT-JEE 2011)

3. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is

(JEE Advanced 2016)

4. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by
- $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
- to form a stable coordination compound. Assume that both the reactions are
- 100°C
- complete. If 1584 g of ammonium sulphate and 952g of
- $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
- are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is _____.
-
- (Atomic weights in
- g mol^{-1}
- : H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

(JEE Advanced 2018)

Answers Key

EXERCISES

Single Correct Answer Type

1. (1) 2. (4) 3. (1) 4. (1) 5. (4)
6. (3) 7. (3) 8. (4) 9. (1) 10. (3)
11. (3) 12. (1) 13. (2) 14. (4) 15. (2)
16. (1) 17. (2) 18. (4) 19. (3) 20. (2)
21. (2) 22. (4) 23. (2) 24. (4) 25. (3)
26. (1) 27. (1) 28. (1) 29. (3) 30. (3)
31. (3) 32. (1) 33. (4) 34. (3) 35. (4)
36. (4) 37. (1) 38. (4) 39. (1) 40. (1)
41. (1) 42. (2) 43. (1) 44. (1) 45. (2)

46. (2) 47. (2) 48. (3) 49. (2) 50. (1)
51. (4) 52. (4) 53. (4) 54. (4) 55. (1)
56. (3) 57. (1) 58. (1) 59. (2) 60. (2)
61. (4) 62. (2) 63. (4)

Multiple Correct Answers Type

1. (1, 4) 2. (2, 4) 3. (1, 2, 3)
4. (2, 4) 5. (1, 2) 6. (1, 2, 3, 4)
7. (1, 2) 8. (1, 2, 3, 4) 9. (1, 2, 3)
10. (2, 3, 4) 11. (1, 3) 12. (2, 3, 4)
13. (1, 2, 4) 14. (1, 2, 4) 15. (2, 4)

Linked Comprehension Type

1. (2) 2. (1) 3. (3) 4. (4) 5. (2)
 6. (1) 7. (2) 8. (4)
 9. (1) T, (2) F, (3) T, (4) F 10. (2) 11. (1)
 12. (2) 13. (1) 14. (2) 15. (3) 16. (3)
 17. (3) 18. (2) 19. (1) 20. (4) 21. (2)
 22. (2) 23. (1) 24. (2) 25. (1) 26. (3)
 27. (2) 28. (1) 29. (2) 30. (3) 31. (2)
 32. (1) 33. (2) 34. (2)

Matrix Match Type

Q.No.	a	b	c	d	e
1.	q	r	s	p	—
2.	s	r	p	q	—
3.	q	p	s	r	—
4.	r	s	q	t	p

Numerical Value Type

1. (4) 2. (4) 3. (2) 4. (3) 5. (4)
 6. (1) 7. (4) 8. (4) 9. (1) 10. (1)
 11. (1) 12. (4) 13. (1) 14. (2) 15. (3)
 16. (3) 17. (2)

ARCHIVES**JEE Advanced****Single Correct Answer Type**

1. (2)

Multiple Correct Answers Type

1. (1, 3, 4)

Linked Comprehension Type

1. (3) 2. (1)

Numerical Value Type

1. (6) 2. (5) 3. (6) 4. (2992)

4

Atomic Structure

OVERVIEW

1. **Atom:** John Dalton in 1880 proposed that matter is composed of very minute and indivisible particles, called atoms.

2. a. Electron was discovered in cathode ray experiment. **Cathode rays** (discovered by William Crookes) are produced in the discharge tube at very low pressure (0.01 mm Hg) and at 10,000 V potential.

They can be deflected in electric and magnetic field which shows that they are negatively charged. Particle nature of cathode rays was proved by (i) their ability to cause mechanical motion, (ii) photo-electric effect, and (iii) Compton effect.

Cathode rays consist of negatively charged particles with negligible mass.

b. The charge on an electron (-1.602×10^{-19} coulomb or -4.8×10^{-10} esu) was determined by **Mullikan** in his oil drop experiment.

c. Actual mass of an electron (9.11×10^{-31} kg) was calculated by **J.J. Thomson**.

d. The **specific charge** (e/m) ratio of electrons (cathode rays) was determined by **Thomson** as 1.76×10^8 coulomb/g. The specific charge of electron decreases with increase in its velocity because increase in velocity increases the mass of electron. The e/m ratio of electron was found to be independent of the nature of gas and electrode used. Thus, electrons are present in all atoms or these are fundamental constituents of all kinds of matter.

e. Radius of the electron is found to be 42.8×10^{-15} m.

f. Density of electron is found to be 2.17×10^{-17} g/cm³.

g. Mass of one mole of electron is nearly 0.55 mg.

h. Charge on one mole of electron is ≈ 96500 coulomb or 1 Faraday.

3. **The proton:**

a. Proton was discovered in the anode ray experiment.

b. Anode rays, also called as canal rays or positive rays, were discovered by **E. Goldstein**.

Anode rays contain material particles obtained by the removal of one or more electrons from the gaseous atoms/molecules present in the tube.

The positively charged particles present in the anode rays produced when hydrogen gas is present in the discharge tube were called protons (proton = first particle) by Rutherford. The specific charge on the anode

rays was found to be maximum when gas present in the discharge tube was hydrogen.

c. Charge on a proton is $+1.602 \times 10^{-19}$ coulomb.

d. Mass of a proton is found to be 1.673×10^{-24} g or 1.673×10^{-27} kg.

e. Mass of 1 mole of proton is nearly 1.007 g.

f. The **specific charge of a proton** is 9.58×10^4 coulomb/g. However, the specific charge of the anode rays is not constant. It varies from particle to particle in a discharge tube (containing any gas other than H₂) depending upon the number of electrons lost. Specific charge on anode ray particles also changes with the nature of the gas in the tube. It is because different gases have different atomic masses. It is maximum when gas present in the discharge tube is hydrogen.

g. The volume of a proton is nearly 1.5×10^{-38} cm³.

h. Charge on 1 mole of proton is ≈ 96500 coulomb or 1 Faraday.

4. **The neutron:**

a. Neutron was discovered by **James Chadwick** in 1932.

b. Neutron is slightly heavier (0.18%) than proton. Mass of neutron is 1.008665 amu or 1.675×10^{-24} g.

c. Specific charge of a neutron is zero.

d. Density of a neutron is 1.5×10^{14} g/cm³.

e. Mass of 1 mole of neutron is nearly 1.0087 g.

f. Of all the elementary particles present in an atom, neutron is the heaviest and least stable particle. Isolated neutron is unstable and disintegrates into electron, proton and neutrino.

5.

Name	Mass	Charge	e/m
Electron (e)	9.1×10^{-31} kg	-1.602×10^{-19} C	1.76×10^8 C/g
	or 5.5×10^{-4} amu	or -4.8×10^{-10} esu	
Proton (p)	1.673×10^{-27} kg	$+1.602 \times 10^{-19}$ C	9.58×10^4 C/g
	or 1.007 amu	or $+4.8 \times 10^{-10}$ esu	
Neutron (n)	1.675×10^{-27} kg	neutral	zero

The mass of electron given above is the rest mass. It is $1/1837$ times the mass of a hydrogen atom. The atom of electron moving with a velocity v is given as:

$$m = \frac{m_{\text{rest}}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

It is clear that the mass of electron moving with velocity of light is infinite.

6. Some data about the nucleus:

- a. The size of nucleus is measured in **Fermi** (1 Fermi = 10^{-13} cm). The radius of nucleus is of the order of 1.5×10^{-13} cm to 6.5×10^{-13} cm, i.e., 1.5 to 6.5 Fermi. In general, the radius of the nucleus (r_n) is given by the following relation.

$$r_n = r_0 \times A^{1/3}$$

where A is the mass number and r_0 is a proportionality constant whose value is 1.4×10^{-13} cm.

- b. The **volume** of the nucleus is about 10^{-39} cm³ and that of atom is 10^{-24} cm³, i.e., volume of the nucleus is 10^{-15} times that of an atom.
- c. The density of the nucleus is of the order of 10^{14} g cm⁻³ or 10^8 tonnes cm⁻³. If nucleus is assumed to be spherical, its density may be determined as follows.

$$\text{Density} = \frac{\text{Mass of the nucleus}}{\text{Volume of the nucleus}} = \frac{\text{Mass number}}{6.022 \times 10^{23} \times \frac{4}{3} \pi r^3}$$

Here r is the radius of the nucleus.

- d. Nucleus contains neutrons and protons, and hence these particles collectively are also referred to as **nucleons**.

7. Some other sub-atomic particles:

In addition to the above fundamental particles, some uncommon sub-atomic particles have also been postulated.

- a. **Positrons:** These are the positive counterpart of the electrons. These were discovered by **Anderson** in 1932. These are highly unstable and combine with electrons producing γ -rays (energy radiations).
- b. **Neutrinos and antineutrinos:** These are the particles of small mass (≈ 0) and zero charge. These were postulated by **Fermi** in 1934.
- c. **Pi-mesons (pions) and μ -mesons (muons):** These are the particles having a mass intermediate between that of the electron and the proton. The positively and negatively charged mesons were postulated by **Yukawa** in 1935. Neutral mesons (π) were postulated by **Kemmer** to account for the binding forces between the nucleons.

8. Rutherford's atomic model:

The credit for giving first successful model about the arrangement of electrons, protons and neutrons goes to **Rutherford**. His model was based upon the result of alpha-ray scattering experiments. He postulated that atom consists of two parts (a) **nucleus** and (b) **extra nuclear part**.

The **nucleus** is a rigid dense central core which carries a positive charge and the entire mass of the atom and the **extra nuclear part** is an empty space around the nucleus where electrons are revolving in circular orbits. It contributes to the volume of an atom.

- a. Atom is spherical and most of the space in it is empty.
- b. The electrons in extra nuclear part revolve with a very high speed. The centrifugal force for their circular motion is provided by positively charged nucleus. The force of attraction between nucleus and electron is balanced by this force.

This model however fails to explain the **stability of atoms** and **line spectrum of hydrogen**.

9. **Atomic number (Z)** = Number of electrons
= Number of protons

10. **Mass number (A)** = Atomic number + Number of neutrons
= Number of protons + Number of neutrons

11. **Isomorphous:** The two different types of compounds which contain same crystalline structures are called **isomorphous** and this property is called **isomorphism**.

12. **Isotopes:** Atoms of same element having different mass numbers e.g., (${}_1\text{H}^1$, ${}_1\text{D}^2$, ${}_1\text{T}^3$).

13. **Isobars:** Atoms of different elements having same mass numbers, e.g., ${}_6\text{C}^{14}$, ${}_7\text{N}^{14}$.

14. **Isotones:** Atoms of different elements having same number of neutrons, e.g., ${}_1\text{H}^2$ and ${}_2\text{He}^3$.

15. **Isoelectronic:** Atoms of different element having same number of electrons, e.g., N^{3-} , O^{2-} , F^- etc.

16. **Isodiaphers:** The element which have the same value of $(n - p)$ and nuclides and their decay products after α -emission are called isodiaphers.

17. **Isosters:** Molecules having same number of atoms and same number of electrons, e.g., CO_2 , N_2O .

18. **Electromagnetic radiations:** According to the **electromagnetic wave theory**, the energy is emitted from any source continuously and consists of electric and magnetic fields oscillating perpendicular to each other and to the direction of propagation.

Electromagnetic radiation is a form of energy transported in the forms of waves.

These are radiations which are associated with both electric and magnetic fields. All forms of electromagnetic radiations travel in space in the form of waves with the velocity of light.

A wave is a sort of disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. Every wave has five characteristics, viz., wavelength, frequency, velocity, wave number and amplitude.

- a. **Wavelength (λ):** The distance between two neighbouring troughs or crests is known as wavelength. It is denoted by λ and is expressed in cm, nanometres (nm) or (Angstrom) (\AA) units. $1 \text{ \AA} = 1 \times 10^{-1} \text{ nm} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$. It determines the colour of a beam of visible light.

The seven colours of white light have the following wavelengths (λ) associated with them.

Colours	Violet	Indigo	Blue	Green	Yellow	Orange	Red
Wavelength in (Å)	3800–4300	4300–4600	4600–5000	5000–5600	5600–5950	5950–6200	6200–6700

- b. **Frequency (ν):** The number of times a wave passes through a given point in one second is called the frequency of the wave. It is denoted by ν (nu) and is expressed in cycles per second (cps) or hertz (Hz). $1 \text{ Hz} = 1 \text{ cps}$. The frequency of a wave is inversely proportional to its wavelength, i.e.,

$$\nu \propto \frac{1}{\lambda}$$

- c. **Velocity (c):** The distance travelled by the wave in one second is called its velocity. It is denoted by c . Mathematically,

$$c = \nu\lambda \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

All types of electromagnetic radiations travel through space with the same velocity i.e., $3 \times 10^{10} \text{ cm s}^{-1}$, $3 \times 10^8 \text{ ms}^{-1}$ or $186,000 \text{ miles s}^{-1}$. However, different types of radiations have different wavelengths and, therefore, different frequencies.

- d. **Wave number ($\bar{\nu}$):** It is defined as the number of wavelengths per cm (or per metre) and is equal to the inverse of wavelength expressed in centimetres. It is denoted by $\bar{\nu}$ and is generally expressed in cm^{-1} (or m^{-1}).

$$\bar{\nu} = \frac{1}{\lambda}$$

Now since $\nu = \frac{c}{\lambda} \therefore \bar{\nu} = \frac{\nu}{c}$

- e. **Amplitude (a):** It is the height of the crest or depth of trough of a wave and is denoted by a . It determines the intensity or brightness of the beam of light.

19. Spectrum:

When sunlight is passed through a prism it splits into seven different colours. This process is called dispersion and the pattern of bands obtained is called spectrum.

- The spectrum obtained by dispersion of ordinary light is continuous spectra and has seven bands of colours (**VIBGYOR**) merging into one another.
- The *emission spectrum* is obtained by passing radiations, emitted by the excited atoms, through the prism. It consists of bright lines against a dark background. It is characteristic of electronic environment of atoms and hence is known as **finger prints of atoms**.
- An *absorption spectrum* is obtained by analysing solar light emerging out of solution of a substance. It comprises dark lines/bands in an otherwise continuous spectrum.
- Electromagnetic spectrum** is the pattern of arrangement of different types of electromagnetic radiations in the order of increasing wavelength (or decreasing

frequency). The arrangement of various radiations in the increasing order of their wavelength or decreasing order of their frequencies is:

cosmic rays < γ -rays < X-rays, < ultraviolet rays < visible light < infrared radiations < microwaves < radiowaves.

- The radius of the nucleus is approximately 10^{-5} times the radius of the atoms. Volume of the nucleus of an atom is about 10^{-15} times the volume of the atom.
- Elements give line spectra. The line spectrum is characteristic of the excited atom producing it. No two elements have identical line spectrum.
- The line spectrum results from the emission of radiations from the atoms of the elements and is therefore called as atomic spectrum.
- Atoms give line spectra (known as atomic spectrum) and the molecules give band spectra (known as molecular spectrum).
- The negative potential at which the photoelectric current becomes zero is called cut off potential or, stopping potential.
- When energy or frequency of scattered ray is lesser than the incident ray, it is known as **Compton effect**.
- The instrumental used to record solar spectrum is called **Spectrometer** or **Spectrograph** developed by **Bunsen and Kirchhoff** in 1859.
- Photoelectric effect:**

In 1887, **H. Hertz** performed an experiment, when a beam of light of **sufficiently high frequency** is allowed to strike a metal surface in vacuum, electrons are rejected from the metal surface. This phenomenon is known as **photoelectric effect** and the ejected electrons as **photoelectrons**. The energy of photoelectrons is proportional to the frequency of the radiation falling upon the metal surface and the number of photoelectrons emitted per second is proportional to the intensity of the incident radiation. Following observations are made regarding photoelectric effect.

- Light of any frequency is not able to cause emission of electrons from the metal surface. There is certain minimum frequency, called the **threshold frequency**, which can just cause the ejection of electrons. The kinetic energy of the photoelectrons increases linearly with the frequency of the incident light. If the frequency is decreased below a certain critical value (threshold frequency, ν_0), no electrons are ejected at all.
- An increase in the intensity of incident light does not increase their rate of emission.
- Einstein's explanation of photoelectric effect:** The photoelectric effect can be explained on the basis of quantum theory.

When this photon of light strikes a metal surface, it imparts its entire energy to the electron. This energy helps in overcoming the attraction between the electrons and the nucleus. If the frequency of light is less than the threshold frequency, there will be no ejection of the electron. If, however, the frequency of light is more than threshold frequency, some of the energy will be required to remove the electron from the atom and the extra energy (excess to that the threshold energy) gives the electron the kinetic energy, i.e., $\frac{1}{2}mv^2$. Thus,

$$E(\text{Total}) = E_0(\text{threshold} + \text{kinetic energy})$$

$$(h\nu = h\nu_0 + \frac{1}{2}m_e v^2) \quad (\nu_0 = \text{Threshold frequency})$$

or

$$h\nu = W_0 + \frac{1}{2}m_e v^2 \quad W_0 = \text{Work functional}$$

28. Energy of photon $E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$

h is Planck's constant,

$$h = 6.626 \times 10^{-34} \text{ J s or } 6.626 \times 10^{-27} \text{ erg s}$$

$$\begin{aligned} E &= \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{1.602 \times 10^{-19} \text{ J eV}^{-1}} \right) \frac{1}{\lambda} \\ &= \frac{12.40 \times 10^{-7}}{\lambda} \text{ eV m} \\ &= \frac{1240 \times 10^{-9}}{\lambda} = \frac{1240 \text{ eV nm}}{\lambda \text{ nm}} \end{aligned}$$

If the value of λ is in nm, then $\frac{hc}{\lambda} = \frac{1240 \text{ eV}}{\lambda}$

or

For solving question in photoelectric effects, the value of hc in eV is taken to be 1240.

29. Average atomic weight = % Abundance of isotope (I) \times Relative atomic mass + % Abundance of isotope (II) \times Relative atomic mass

$$\times \frac{\text{Relative atomic mass}}{100}$$

30. Hydrogen spectrum:

It comprises five series of lines namely *Lyman* (U.V.), *Balmer* (visible), *Paschen* (I.R.), *Brackett* (I.R.) and *Pfund* (I.R.). The wave number ($\bar{\nu}$) of each line in the spectrum is given by the following expression

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}$$

Z = nuclear charge, e.g., for

$$\text{H}_2^{\oplus}, Z=1, \text{He}^{\oplus}, Z=2, \text{Li}^{2+}, Z=3$$

Here, R_H = Rydberg's constant; Z = atomic number or charge on nucleus (for hydrogen, $Z=1$); n_1, n_2 = electronic levels involved in transition. The value of R_H is mathematically expressed as

$$R_H = \frac{2\pi^2 me^4}{ch^3} = 109677.76 \text{ cm}^{-1} \text{ or } 1.0 \times 10^7 \text{ m}^{-1}$$

For hydrogen, frequency (ν) of each line can be calculated as follows.

$$\nu = 3.29 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ s}^{-1}$$

For Lyman series ($n_1 = 1$ and $n_2 = 2, 3, 4, \dots$), for Balmer Series ($n_1 = 2$ and $n_2 = 3, 4, 5, \dots$), for Paschen series ($n_1 = 3$ and $n_2 = 4, 5, 6, \dots$) and so on.

31. **Moseley's law:** $\sqrt{\nu} = a(Z - b)$, where ν is frequency of X-rays given out by metal of atomic number Z .

32. Each element has its own characteristic emission spectrum and absorption spectrum.

33. $\Delta E = E_{n_2} - E_{n_1}$; $n_2 > n_1$ (emission spectra)

$\Delta E = E_{n_2} - E_{n_1}$; $n_2 < n_1$ (absorption spectra)

34. Number of spectral lines from ground state to n orbit is

$$\frac{n(n-1)}{2}$$

35. Number of spectral lines from n_1 and n_2 orbit is

$$\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$$

36. The energy associated with K-shell is least and increases as we pass to L, M, N, O, P... etc.

37. The radii of orbit when $n = 1$ is equal to 0.529 Å. This is known as Bohr's orbit.

38. The intensities of spectral lines decreases with increase in the value of n . For example, the intensity of first Lyman line ($2 \rightarrow 1$) is greater than second line ($3 \rightarrow 1$) and so on.

39. In Balmer series of hydrogen spectrum the first line ($3 \rightarrow 2$) is also known as L_α line. The second line ($4 \rightarrow 2$) is L_β line. The line from infinity energy shell is called limiting line.

40. Angular momentum in an orbit (mvr) is

$$\frac{nh}{2\pi} = n\hbar \left(\text{where } \hbar = \frac{h}{2\pi} \right)$$

41. a. Radius of electron in n th orbit

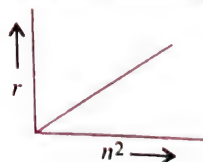
$$r_n = \frac{n^2 h^2}{4\pi^2 K m e^2 Z}$$

where (h, π, m and e all are constants.

$$\therefore K = \frac{h^2}{4\pi^2 m e^2} = (\text{constant}) = 0.529 \text{ Å} = 0.529 \times 10^{-10} \text{ m}$$

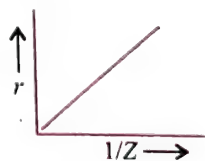
$$r_n = 0.529 \text{ Å} \times \frac{n^2}{Z} \quad \text{or} \quad 0.0529 \text{ nm} \times \frac{n^2}{Z}$$

Thus, the radius of atom goes on increasing as the number (n) of energy levels in the atom goes on increasing as shown:



$$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$$

b. If n is constant, then



$$\frac{r_1}{r_2} = \frac{Z_2}{Z_1}$$

Putting $n = 1, 2, 3, 4$ etc., the radii of the first five orbits of hydrogen atom are:

Orbit (n)	1	2	3	4	5
Radius (Å)	0.529	2.116	4.761	8.464	13.225

42. Energy of electron in Bohr's n th orbit:

a. The energy of an electron is negative since the maximum energy of an electron at infinity is zero. As the electron gets closer to the nucleus (as n decreases), energy decreases and the most negative energy value is given by $n = 1$, i.e., ground state.

b. **Potential energy (PE):** This energy is released due to electrostatic attractive forces between electrons and protons. So the potential energy of electrons is negative.

$$PE = -\frac{Ze^2}{r}$$

c. **Kinetic energy (KE):** It is positive due to the velocity of electron.

$$KE = \frac{1}{2}mv^2 = \frac{1}{2} \frac{Ze^2}{r} \Rightarrow KE = -\frac{1}{2} PE$$

d. **Total energy (E_{Total}):**

Total energy = Kinetic energy + potential energy

$$E_{\text{Total}} = KE + PE$$

$$= \frac{1}{2} \frac{Ze^2}{r} - \frac{Ze^2}{r} = -\frac{1}{2} \frac{Ze^2}{r}$$

$$\therefore E_{\text{Total}} = -KE$$

$$PE = 2 \times E_{\text{Total}}$$

e. **Calculation of energy:**

$$E_T = -\frac{1}{2} \frac{Ze^2}{r} \text{ (Put the value of } r \text{)}$$

$$E_T = -\frac{Z^2}{n^2} \times \frac{2\pi^2 me^4}{h^2}$$

$$= -K \frac{Z^2}{n^2}$$

$$\text{where } K = \frac{2\pi^2 me^4}{h^2} = \text{constant}$$

\therefore Energy of electron in n th orbit (E_n):

$$E_n = -K \frac{Z^2}{n^2} = -13.6 \text{ eV atom}^{-1} \text{ (when } Z = 1, n = 1 \text{)}$$

$$= -2.179 \times 10^{-11} \text{ erg atom}^{-1}$$

$$\text{or } -21.72 \times 10^{-12} \text{ erg atom}^{-1}$$

$$= -313.6 \text{ kcal mol}^{-1}$$

$$= -1312.0 \text{ kJ mol}^{-1}$$

$$= -21.75 \times 10^{-19} \text{ J atom}^{-1}$$

Note: Units: a. $1 \text{ erg} = 10^{-7} \text{ J} = 6.2419 \times 10^{11} \text{ eV}$

b. $1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg} = 23.06 \text{ kcal mol}^{-1}$

c. $1 \text{ J} = 6.2419 \times 10^{18} \text{ eV}$

d. $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

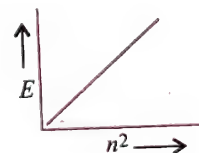
e. $1 \text{ kcal} = 4.184 \text{ kJ}$

$$E_n = -13.6 \text{ eV} \times \frac{Z^2}{n^2}$$

$$E_1 \text{ for } H_2^+ \text{ like atom} = E_1 \text{ for } H_2^+ \times Z^2$$

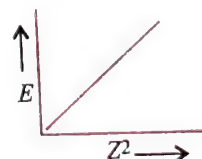
f. If Z is constant, then $E_n \propto -\frac{1}{n^2}$

Therefore, the energy of electron increases as the number of orbits increases.



$$\frac{E_1}{E_2} = \frac{n_2^2}{n_1^2}$$

g. If n is constant, then $E \propto -Z^2$



$$\frac{E_1}{E_2} = \frac{Z_1^2}{Z_2^2}$$

$$\text{h. } E_n = \frac{Z^2}{n^2} \times Rhc$$

$$\text{i. Kinetic energy (KE)} = \frac{Z^2}{n^2} \times Rhc$$

$$\text{j. Potential energy (PE)} = 2 \left(\frac{-Z^2}{n^2} \times Rhc \right)$$

k. Quantisation of electronic energy levels of hydrogen atom

Quantum state	Energy	Separation energy	Excitation energy
$n = \infty$	0	0	$0 - (-13.6) = 13.6 \text{ eV}$
$n = 5$	$\frac{-13.6}{5^2} = -0.54$	0.54	$-0.54 - (-13.6) = 13.06 \text{ eV}$
$n = 4$	$\frac{-13.6}{4^2} = -0.85$	0.85	$-0.85 - (-13.6) = 12.75 \text{ eV}$
$n = 3$ Second excited state	$\frac{-13.6}{3^2} = -1.51$	1.51	$-1.51 - (-13.6) = 12.1 \text{ eV}$
$n = 2$ First excited state	$\frac{-13.6}{2^2} = -3.4$	3.4	$-3.4 - (-13.6) = 10.2 \text{ eV}$
$n = 1$ Ground state	-13.6 eV	13.6 eV	0 eV

l. Energy of electron in a H-atom in a different energy levels

Energy level	$E \text{ (eV atom}^{-1}\text{)}$	$E \text{ (K cal mol}^{-1}\text{)}$	$E \text{ (kJ mol}^{-1}\text{)}$	$E \text{ (V atom}^{-1} \text{ or J atom}^{-1}\text{)}$
∞	0	0	0	0
5	-0.54	-12.5	-52.5	-0.87×10^{-19}
4	-0.85	-19.6	-82.0	-1.36×10^{-19}
3	-1.51	-38.84	-145.7	-2.41×10^{-19}
2	-3.4	-78.4	-327.9	-5.42×10^{-19}
1	-13.6	-313.5	-1311.8	-21.72×10^{-19}

m. If v is the velocity of electron in 1st orbit ($n = 1$) of hydrogen atom ($Z = 1$), and c is the velocity of light, then,

$$\frac{v}{c} = \frac{2\pi ke^2}{h} \times \frac{1}{c} = \frac{1}{137}$$

$$v = \frac{c}{137}$$

$$\left[\text{Note: } \frac{2\pi ke^2}{ch} = \alpha \text{ (Fine structure constant)} = \frac{1}{137} \right]$$

Velocity of electron in first orbit of hydrogen is $\frac{1}{137}$ th of the velocity of light (c)

n. Number of revolution made per second in n^{th} orbit

$$= \frac{\text{Velocity of electron in } n^{\text{th}} \text{ orbit}}{\text{Circumference of } n^{\text{th}} \text{ orbit}}$$

$$= \frac{V_n}{2\pi r_n}$$

where r_n is the radius of the n^{th} orbit

o. Number of waves per revolution made by an electron

$$= \frac{2\pi r}{\lambda}$$

$$= \frac{2\pi r}{h/mv} \quad \left(\because \lambda = \frac{h}{mv} \right)$$

$$= \frac{2\pi}{h} \times mvr$$

$$= \frac{2\pi}{h} \times \frac{nh}{2\pi} \quad \left(\because mvr = \frac{nh}{2\pi} \right)$$

$$= n$$

p. Energy can be expressed in terms of units of wave number i.e., cm^{-1} or m^{-1} . The energy equivalent of 1.00 cm^{-1} (or $1.00 \times 10^2 \text{ m}^{-1}$) can be calculated as follows.

$$\text{i. } E(\text{per photon}) = h\nu = hc/\lambda = hc \bar{\nu}$$

$$= (6.62 \times 10^{-34} \text{ J s}) \cdot (3.00 \times 10^8 \text{ m s}^{-1}) \cdot (1.00 \times 10^2 \text{ m}^{-1})$$

$$= 1.99 \times 10^{-23} \text{ J}$$

$$\text{ii. } E(\text{per mol}) = \frac{(1.99 \times 10^{-23} \text{ J}) \times (6.02 \times 10^{23} \text{ mol}^{-1})}{1000 \text{ J kJ}^{-1}}$$

$$= 1.20 \times 10^{-2} \text{ kJ mol}^{-1}$$

43. Velocity of electron in n^{th} orbit (V_n)

$$V_n = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m s}^{-1}$$

44. Number of fine lines of a line = $n_1 \times n_2$

45. Possible transition for a jump from n_2 to $n_1 = \Sigma(n_2 - n_1)$

46. **de Broglie principle:** An electron exhibits wave-like as well as particle characteristics.

$$\lambda = \frac{h}{p} = \frac{h}{mv}; p = \text{momentum}$$

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ Js}$$

- de-Broglie's equation and uncertainty principle are applicable to all the moving bodies and they are significant only in case of particles like atoms and subatomic particles such as electrons, protons etc.
 - de-Broglie's equation and uncertainty principle have no significance for macroscopic particles and can be neglected in everyday life.
 - de-Broglie's equation explains only systems in which energy of particle is described only in terms of speed. In the case of electrons where energy is partly due to speed and partly due to position the de-Broglie's theorem is used as an approximation.
 - Limitation of de-Broglie concept:** *de-Broglie concept applies quantitatively only to particles in a force free environment. Thus, it cannot be applied directly to an electron in an atom, where the electron is subjected to the attractive forces of the nucleus.*
47. **Heisenberg's uncertainty principle:** It is impossible to measure simultaneously the exact position and velocity of a small moving body like an electron.

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \left(\frac{h}{4\pi} = 0.525 \times 10^{-34} \text{ Js} \right)$$

48. **Schrödinger wave equation:** Erwin Schrödinger developed a new model of atom in 1920. He incorporated the idea of quantisation, and the conclusions of **de-Broglie's principle** and **Heisenberg's principle** in his model. In this model, the behaviour of the electron in an atom is described by the mathematical equation as:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

(Here x , y and z are three space coordinates, m = mass of electron, h = Planck's constant, E = Total energy, V = potential energy and ψ = wave function of electron wave)

The above expression can also be expressed as

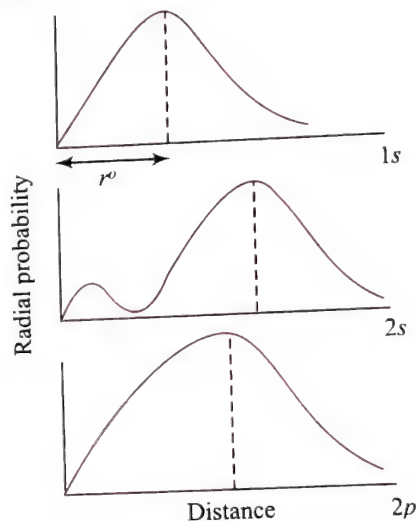
$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

Here ∇^2 is known as **Laplacian operator**.

The permitted solutions of Schrödinger equation are known as *wave functions* which corresponds to a definite energy state called **orbital**. Thus, the discrete Bohr orbits are replaced by orbitals i.e., three-dimensional geometrical volumes where there is maximum probability of locating the electrons. In simple words, the equation may be interpreted by stating that a body/particle of mass m , total energy (E), potential energy (V), has wave like characteristics associated with it, with an amplitude given by wave function ψ .

49. The wave function of an electron (ψ) in the field of nucleus of an atom is called atomic orbital. It is a three-dimensional amplitude of electron wave.

50. $\psi^2 dV$ is the probability of finding the electron in a small volume element dV surrounding the nucleus of an atom.
51. The particular value of ψ are called *eigen functions* and the values of energies which correspond to these are called *eigen values*.
52. The eigen function for an electron is called *atomic orbital*.
53. Wave equation is applicable to both atoms and also molecules, but the treatment is complicated for molecules.
54. On solving the equations we find regions in space where ψ is positive or negative but ψ^2 (probability density) is always positive.
55. **Probability distribution:** In wave mechanics a moving electron is represented by wave function, ψ . It has no physical significance and refer to the amplitude of electron wave. However, ψ^2 is a significant term and gives intensity of electrons. The probability of finding an electron in a given volume is understood best in the form of **radial probability distribution curves**. The distance of maximum radial probability is radius of an atom. There are two humps for $2s$ orbital which means that the $2s$ electron penetrates a little closer to nucleus. The point at which radial probability becomes zero is known as nodal point.



56. The radius of maximum probability of $1s$ electron is 0.529 \AA .
57. The number of regions of maximum probability for $1s$, $2p$, $3d$ and $4f$ is one. For $2s$, $3p$, $4d$ and $5f$ these are two and so on.
58. The small humps indicate that the electron has a tendency to penetrate closer to the nucleus.
59. In between the regions of maximum probability there is region of zero electron density called *node*. More is the number of nodes more is the energy of an orbital.
60. In these curves, the first orbital of each type ($1s$, $2p$, $3d$, $4f$) has one region of maximum probability and no node. Whereas the first orbital of each type ($2s$, $3p$, $4d$, $5f$) has two regions of maximum probability and one node and so on.
61. **Shapes of orbitals:**
- Boundary surface diagram:** It is not possible to draw a shape that bounds a region in which the probability of finding the electron is 100%. A surface can be drawn however, that connects the points of equal probability and that encloses a volume in which the probability of finding the electron is high (for example 95%). Such a representation is called a boundary surface diagram.

As discussed earlier, each orbital is to be denoted by a wave function (ψ). The value of ψ is function of

- distance from the nucleus (radial part) and
- angle θ and ϕ (angular part).

The radial part gives the size of an orbital whereas the angular part tells about the shape of orbitals.

- The s-orbitals** are spherical in shape and have symmetrical orientation. For all s-orbitals there are $(n - 1)$ number of spherical nodes (a three-dimensional space about the nucleus where probability is zero).
- The p-orbitals** are dumb-bell in shape with two lobes of same size on each side of the nucleus. The two lobes are separated by a plane in which the probability of electron is zero. It is called nodal plane. These orbitals are resolved in three planes and designated as p_x , p_y and p_z .
- The d-orbitals** are five in number. Four of these have a double dumb-bell shape ($d_{x^2-y^2}$, d_{xy} , d_{yz} , d_{zx}) whereas the fifth (d_z^2) is dumb-bell in shape with a collar of high electron density along xy plane (doughnut).
- The f-orbitals**: They are seven in number they are divided into two sets as shown:

The general set		The cubic set	
1. fx^2	5. fz^3 or fx^3 or fy^3 (i) fx^3 same as fz^3 except lies along the x-axis (ii) fy^3 same as fz^3 except lies along the y-axis	2. $fx(x^2 - 3y^2)$	6. xyz
3. $fy(3y^2 - x^2)$ same as $x(x^2 - 3y^2)$ except lies along the y-axis.		4. $fz(x^2 - y^2)$ or $fxyz$ same as the corresponding orbitals in cubic set	
		7. $fz(x^2 - y^2)$ or $fy(z^2 - x^2)$ or $fz(x^2 - y^2)$. Same as xyz but rotated at 45° about x, y, z axes.	

- Quantum numbers**: The set of four integers required to define the state of electron in an atom are called quantum numbers. The set of quantum numbers are:

- Principal quantum number (n)**: It was proposed by Bohr and is used to explain the appearance of main lines in the atomic spectrum of an element.

It determines the main energy level, the average distance of the electron from the nucleus and the magnitude of energy of the electron. It is denoted by n which can have integral values excluding zero such as 1, 2, 3... also denoted as K, L, M etc.

The maximum number of electrons in any principal shell is given by $2n^2$ where n is principal quantum number.

- Azimuthal (or subsidiary) quantum number (l)**: It was proposed by Sommerfeld. It is also known as orbital or angular momentum quantum number and is denoted by ' l '.

$$\text{Orbital angular momentum} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

It tells us about the subenergy shell (l) of the electron. The values of l depend upon principal quantum number,

n . For a given n value, l can have values starting from 0 to $(n - 1)$, a total of n values. For l values 0, 1, 2, 3, 4... the subshell notations are s, p, d, f, g... respectively. Its value also indicates the shape of the electron cloud or orbital. The maximum number of electrons that can be accommodated in a given sub-energy level is given by $2(2l + 1)$. In a multielectron atom, the energy associated with an electron depends both on n and l .

- Magnetic quantum number (m_l)**: It was proposed by Lande to explain the splitting of lines of atomic spectrum in magnetic field (Zeeman effect) or in the electric field (Stark effect). It is denoted by m_l and its values depend on l values. For a given value of l there can be $(2l + 1)$ values for m ranging from -1 to $+1$ including zero. Each value of m_l corresponds to an orbital in a shell with same l value. Magnetic quantum number describes the orientation of the orbital in space around the nucleus. For a subshell with $l = 0$, there is only one orientation of the orbital, for a subshell with $l = 1$ there are 3 orbitals which can have different orientations so on and so forth.

Number of orbitals in a shell is n^2 .

- Spin quantum number (m_s)**: It was proposed by Uhlenbeck and Goudsmit. Spin quantum number gives an idea about the electron spinning on its axis. Each spinning electron can have two values of spin quantum numbers, which are: $+1/2$ (clockwise spin) and $-1/2$ (anticlockwise spin).

Mathematically, spin angular momentum has a magnitude

$$S = \frac{h}{2\pi} \sqrt{s(s+1)}$$

$$= \frac{\sqrt{3}h}{4\pi} \text{ since } s = \frac{1}{2}$$

Spin quantum number is the only quantum number that has non-integral values and is not derived from Schrödinger's wave equation while other three quantum numbers are derived from wave equation.

- The principal quantum number (n) gives the size of the orbital and energy of the electron. Azimuthal quantum number (l) gives the shape of the orbital.
Magnetic quantum number (m) gives the spatial orientation of the orbital in the magnetic field or the number of orbitals in a subshell.
- The electrons present in the outermost shell are called optical electrons as they are readily excited and hence yield line spectra. The other electrons are called spectator electrons.
- Number of subshells in a main energy level is equal to n .
- Number of orbitals in a main energy level is equal to n^2 .
- Number of orbitals in a subshell is equal to $(2l + 1)$.
- Number of electrons in each orbital is equal to 2.
- Maximum number of electrons in a subshell is equal to $2(2l + 1)$.
- Maximum number of electrons in a main shell is equal to $2n^2$.

75. **Filling of orbitals** (Rules to write electronic configurations): The electrons in various orbitals are filled according to certain rules. An understanding of these rules/principles enables us to write electronic configuration of the element, etc.
76. **Aufbau principle:** It states that electrons are filled in the orbitals in order of increasing energy and the energy of the orbitals is governed by $(n + l)$ rule. In simple words, orbitals of lower energy are filled first followed by orbitals of higher energy.
77. **Pauli's exclusion principle:** It states that no two electrons can have the same value of the four quantum numbers. This implies that no two electrons are alike in an atom or in other words an orbital can accommodate a maximum of two electrons.
78. **Hund's rule:** This rule states that pairing of the electrons in degenerate orbitals, belonging to a particular subshell (i.e., p , d and f), does not take place till each orbital is occupied by a single electron with parallel spin. Degenerate levels have low energy when they are empty, half filled or completely filled. The **anomalies** are observed occurring in a few configurations (particularly transition elements) for example (i) chromium has a configuration of $3d^5 4s^1$ and not $3d^4 4s^2$ and (ii) copper has a configuration of $3d^{10} 4s^1$ and not $3d^9 4s^2$. This is attributable to the extra stability of half filled or completely filled set of degenerate orbitals.
79. **Half filled and fully filled** electronic configuration are stable since they have more symmetry and more exchange energy.
80. All substances have magnetic properties due to magnetic moment associated with electron spin and with orbital angular momentum of the electron.
81. The two electrons in different atomic orbitals are far apart and suffer less electron-electron repulsion than when these occupy same orbital with opposite spins.
82. The energy of atomic orbitals for H-atom is (as the energy depends on the value of n):
 $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$
83. According to **Aufbau** principle, the energy of orbitals (other than H-atom) depends upon $n + l$ value and varies as
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d$.
84. Energy associated with any orbit or orbital decreases as the nuclear charge or atomic number increases.
85. Number of orbitals in a subshell $= 2l + 1$, where l is the azimuthal quantum number. Number of subshells in a main

level is equal to n , where n is the principal quantum number. The possible values of l for these subshells range from 0 to $n - 1$. The total number of orbitals in n th shell can be calculated as follows.

$$\begin{aligned}\text{Total number of orbitals in } n\text{th shell} &= \sum_{l=0}^{n-1} 2l + 1 \\ &= 1 + 3 + 5 + \dots + \{2(n-1) + 1\} \\ &= 1 + 3 + 5 + \dots + 2n - 1\end{aligned}$$

It is an A.P. (Arithmetical Progression) of n terms, where first term, $a = 1$ and common difference, $d = 2$.

$$\begin{aligned}&= \frac{n}{2} [2 \times 1 + (n-1)2] \quad \left[\because S_n = \frac{n}{2} [2a + (n-1)d] \right] \\ &= \frac{n}{2} [2n] = n^2\end{aligned}$$

As each orbital can have at the most two electrons, number of electrons in n th shell $= 2n^2$.

86. In most cases, wave function ψ is a complex quantity of the form $(a + bi)$. As we know these complex quantities has no physical significance. In such cases probability density $|\psi|^2 = a^2 + b^2$ which is real.
87. Total spin $= \pm \left(\frac{1}{2} \times n \right)$
88. Magnetic moment (spin only) of an atom $= \sqrt{n(n+2)}$ BM, where n is number of unpaired electrons.
89. Orbital angular momentum for d orbital is
 $\frac{h}{2\pi} \sqrt{l(l+1)} = \hbar \sqrt{2(2+1)} = \hbar \sqrt{6}$
90. Angular momentum for p orbital $= \frac{h}{2\pi} \sqrt{l(l+1)} = \hbar \sqrt{2}$
91. Angular momentum for f orbital $= \hbar \sqrt{3(3+1)} = 2\sqrt{3} \hbar$
92. **a. Spherical (or radial) nodes:** The spherical surface where the probability of finding an electron is zero is called a spherical or radial node.
 In general, the number of spherical nodes in an orbital $= n - l - 1$.
b. Total number of nodes $= n - 1$
93. **Nodal plane:** The plane in which the probability of finding an electron is zero is called a nodal plane.
 Number of nodal planes for an orbital $= l$
94. **Screening rule:** According to this rule, the electron clouds of the inner completed shell screen (protect) the outer electrons against nuclear attraction. For this reason, the ns , sub-shell is filled prior to the $(n-1)d$ level.

4.1 INTRODUCTION

The existence of atoms has been proposed by ancient Indian and Greek philosophers (400 B.C.) who believed that all matter consisted of very small indivisible particles called atoms. According to them, atoms were the fundamental building blocks of matter. The continued subdivision of matter would yield atoms, which could not be further divided. The word 'atom' was derived from the Greek word 'a tomio' which means in divisible'. These earlier ideas were mere speculations and did not have any experimental basis. These ideas remained dormant for a very long time and were reviewed again by scientists in the 19th century.

In 1808, an English scientist John Dalton formulated a precise definition of the indivisible building blocks of matter known as atoms. His theory, called Dalton's atomic theory, regarded the atom as the ultimate particle of matter. The postulates of Dalton's theory are as follows:

- Every matter is composed of very minute particles called atoms, which take part in chemical reactions.
- Atoms cannot be further subdivided.
- The atoms of different elements differ from each other in their properties and masses, while the atoms of the same element are identical in all respects.
- The atoms of different elements can combine in simple ratios to form compounds. The masses of combined elements represent the masses of combined atoms.
- Atoms can be neither created nor destroyed.

Dalton's atomic theory was able to explain successfully the law of conservation of mass, the law of constant composition, and the law of multiple proportion. However, it failed to explain many properties of atoms and matter. The drawbacks of Dalton's theory are as follows:

- It failed to explain the internal structure of atoms and assumed atoms that have no structure.
- It could not explain how atoms of different elements differ from one another.
- It could not explain how atoms of different elements combine with one another.

4.2 SUBATOMIC PARTICLES

In the end of 19th century, it was discovered that atoms consist of subatomic particles such as electrons, protons, and neutrons. In this unit, we will discuss various subatomic particles and the evolution of the model of the internal structure of atoms.

4.2.1 DISCOVERY OF ELECTRON—CATHODE RAYS

In 1830, Michael Faraday, an English physicist, showed that when electricity is passed through a solution of electrolyte, the electrolyte gets decomposed liberating and depositing matter at the electrodes. This decomposition of an electrolyte by passing electricity is known as electrolysis. Faraday showed that the weights of various elementary substances liberated are proportional to the quantity of electricity passed. This is known as the first law of electrolysis. Faraday also showed that the number of moles of the elementary substances liberated by a fixed quantity of electricity

bears a simple whole number ratio. This is known as the second law of electrolysis. These results suggested some relations between atoms and electricity. Moreover, the laws of electrolysis indicate that atoms involve discrete units of electricity called electrons. The nature of electrons can be clarified by experiments on electric discharge through gases.

In mid 1850s scientists mainly Faraday began to study electrical discharge in a partially evacuated tube known as cathode ray discharge tube. A discharge tube is a long glass tube containing two thin pieces of metal, called electrodes, sealed in it as shown in Fig. 4.1(a).

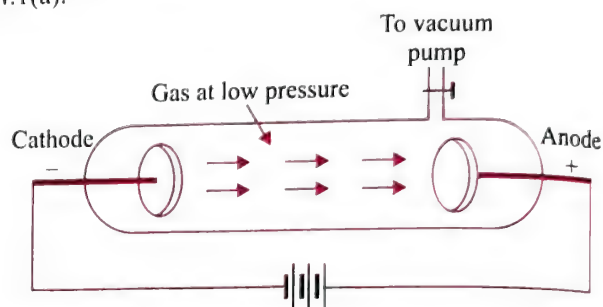


Fig. 4.1 (a) A cathode ray discharge tube

The tube is connected to a vacuum pump to control the pressure of gas inside the discharge tube. When a very high voltage of about 1000 V is applied to the electrodes at either end of the discharge tube and the gas pressure inside the tube is reduced to about 10^{-2} atm, an electric current flows and light is emitted by the gas. The current flows through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These are called cathode rays or cathode ray particles because they start from the cathode and end at the anode. The flow of current from cathode to anode can be further checked by making a hole in the anode and coating the tube behind the anode with a phosphorescence material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed as shown in Fig. 4.1(b).

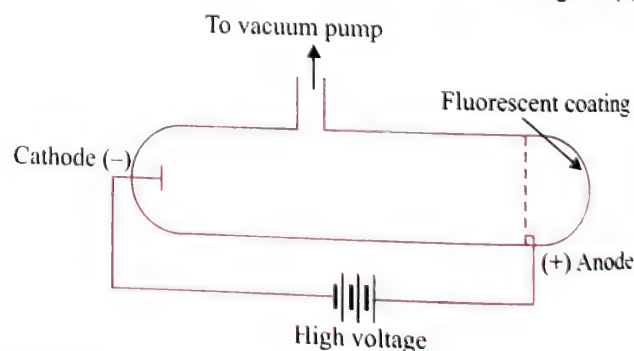


Fig. 4.1(b) A cathode ray discharge tube with perforated anode

The same phenomenon is used in television sets. These rays consist of negatively charged particles called electrons.

4.2.2 PROPERTIES OF CATHODE RAYS

The cathode rays possess the following properties:

- Cathode rays travel in straight lines. An object placed in the path of cathode rays casts a sharp shadow [Fig. 4.1(c)]. It shows that cathode rays travel in straight lines.

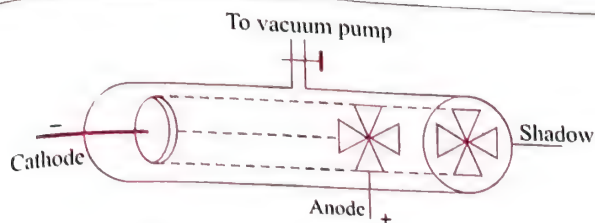


Fig. 4.1 (c) An object placed in the path of cathode rays casts a sharp shadow

- b. **Heating effect:** When cathode rays are focused on a thin metal foil, it gets heated up to incandescence,
- c. Cathode rays consist of material particles. This is indicated by the fact that a light paddle wheel placed in the path of cathode rays starts rotating [Fig. 4.1(d)].

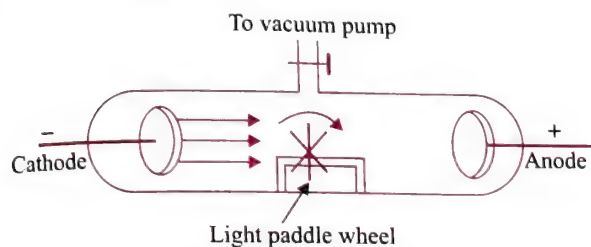


Fig. 4.1 (d) Movement of light paddle wheel

- d. **Effect of electric field:** When an electric field is applied to a stream of cathode rays, they get deflected towards the positive plate [Fig. 4.1(e)]. It shows that cathode rays are themselves negatively charged.

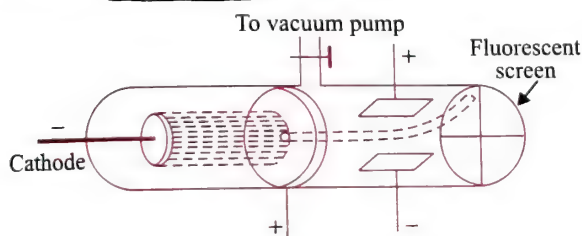


Fig. 4.1 (e) Effect of electric field on cathode rays

- e. **Effect of magnetic field:** When a magnetic field is applied perpendicular to the path of cathode rays, they get deflected in the direction expected for negative particles. This further confirms that cathode rays are negatively charged.

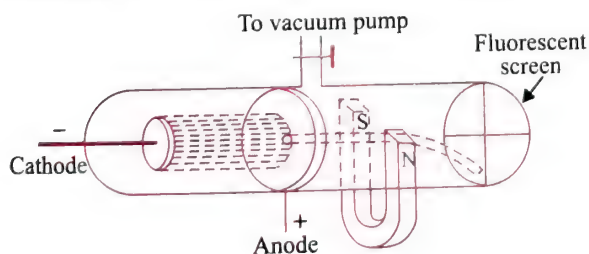


Fig. 4.1 (f) Effect of magnetic field on cathode rays

- f. On striking against the walls of the discharge tube, cathode rays produce faint greenish fluorescence.
- g. Cathode rays ionise the gas through which they pass.
- h. Cathode rays produce X-rays when they are made to fall on metals such as tungsten, copper, etc.
- i. They can penetrate through thin metal foils.

- j. The charge-mass ratio (e/m) of the particles in the cathode is independent of the nature of the gas taken in the discharge tube or the nature of the cathode.

4.3 CHARGE-MASS RATIO (e/m) OF ELECTRONS

In 1897, British physicist Sir J.J. Thomson studied the deflection of cathode rays under the simultaneous application of electric and magnetic fields applied perpendicular to each other as well as to the path of electrons (Fig. 4.2). Thomson showed that the amount of deviation of the particles from their paths in the presence of electrical or magnetic field depends upon the following factors:

- a. **Magnitude of the negative charge on the particle:** The greater the magnitude of the charge on the particle, the greater the interaction with the electric or magnetic field and thus the greater the deflection.
- b. **Mass of the particle:** The higher the mass of the particle, the lesser the deflection, the lighter, the particle, and the greater the deflection.
- c. **Strength of the electric or magnetic field:** The deflection of electrons from their original paths increases with an increase in the voltage across the electrodes or the strength of the magnetic field.

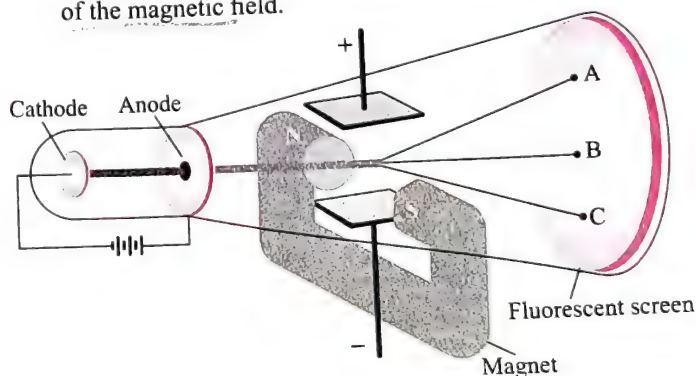


Fig. 4.2 The apparatus to determine the charge to mass ratio of electron

Figure 4.2 shows that when only electric field is applied, the electrons deviate from their paths and hit the cathode ray tube at point A. Similarly, when only magnetic field is applied, the electrons strike the cathode ray tube at point C. On balancing the two fields, the cathode rays strike the fluorescent screen at the same position (i.e., point B) when neither field is applied.

By carrying out an accurate measurement of the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson determined the value of e/m_e as follows:

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1}$$

where m_e is the mass of electron in kilogram and e is the magnitude of the charge on electron in coulomb. Since electrons are negatively charged, the charge on electron is $-e$. The e/m ratio for the particles in the cathode rays is found to be same irrespective of the nature of cathode or the nature of the gas taken in the discharge tube, thus showing that electrons are the basic constituents of all atoms.

4.4 CHARGE ON THE ELECTRON

The charge (e) on an electron was determined by R.A. Millikan in 1909 by an 'oil drop' experiment.

Millikan's oil drop method: In this method, oil droplets in the form of mist, produced by an atomiser, are allowed to enter through a tiny hole in the upper plate of an electrical condenser. The downward motion of these droplets is viewed through a telescope equipped with a micrometer-eye piece. By measuring the rate of fall of these droplets, Millikan measured the mass of oil droplets. The air inside the chamber is ionised by passing a beam of X-rays through it. The electrical charge on these oil droplets is acquired because of collisions with gaseous ions. By measuring the velocity of a given oil droplet as it falls freely under the influence of gravity and then in an electric field, it is possible to calculate the charge (q) on the droplet. The fall of these charged oil droplets can be retarded, accelerated, or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electric charge, q , on the droplets is always an integral multiple of the electric charge, e , that is, $q = n e$, where $n = 1, 2, 3, \dots$

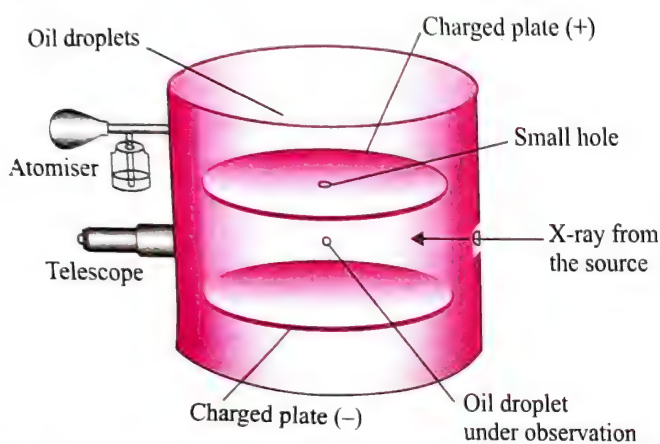


Fig. 4.3. The Millikan oil drop apparatus for measuring charge 'e'. In the chamber, the forces acting on the oil drop are gravitational force, electrostatic force due to electrical field, and a viscous drag force on the moving oil drop

The charge on the electron is found to be 1.6022×10^{-19} C. This is taken as one unit negative charge.

Mass of the electron: The mass of the electron (m_e) is determined by combining the value of charge (e) on the electron with Thomson's value of e/m_e ratio:

Thomson's experiment: $e/m_e = 1.758820 \times 10^8$ C/kg

Millikan experiment: $e = 1.6022 \times 10^{-19}$ C/electron

$$\begin{aligned} \therefore \text{Mass of electron } m &= \frac{e}{e/m_e} \\ &= \frac{1.6022 \times 10^{-19} \text{ C/electron}}{1.75882 \times 10^{11} \text{ C/kg}} \\ &= 9.1094 \times 10^{-31} \text{ kg} \\ &= 9.1094 \times 10^{-28} \text{ g} \end{aligned}$$

The mass of electron is very small and is approximately $1/1837$ times the mass of an atom of hydrogen.

Note: In Millikan's oil drop method, electrons get charged at the nozzle of the atomiser due to friction. When these negatively charged oil droplets are irradiated with X-rays, the charge on the oil drops decreases. This is because, X-rays ionise the gas and negatively charged oil droplets attract the positively charged ions produced.

ILLUSTRATION 4.1

An oil drop has 6.39×10^{-19} C charge. How many electrons does this oil drop has?

Sol. The charge on an oil drop is 6.39×10^{-19} C. The charge on the electron calculated by the Millikan oil drop method is 1.6×10^{-19} C.

$$\text{Hence, the number of electrons are } \frac{6.39 \times 10^{-19}}{1.6 \times 10^{-19}} \approx 4$$

There are four electrons on the oil drop.

ILLUSTRATION 4.2

In an oil drop experiment, the following charges (in arbitrary units) were found on a series of oil droplets. Calculate the magnitude of the charge on the electron.

$$3 \times 10^{-15}, 9 \times 10^{-15}, 12 \times 10^{-15}, 18 \times 10^{-15}$$

Sol. The magnitude of the charge should be smallest and other charges should be integral multiples of that smallest charge. So, in the problem, the smallest charge is 3×10^{-15} and is also an integral multiple of this charge.

4.5 DISCOVERY OF PROTON—ANODE RAYS OR CANAL RAYS

In 1886, Goldstein discovered a new type of rays in the discharge tube. He used a perforated cathode (as shown in Fig. 4.4) in the discharge tube. On passing electrical discharge at low pressure, he observed a new type of rays streaming behind the cathode. These rays were named anode rays or canal rays. These rays consist of positively charged particles.

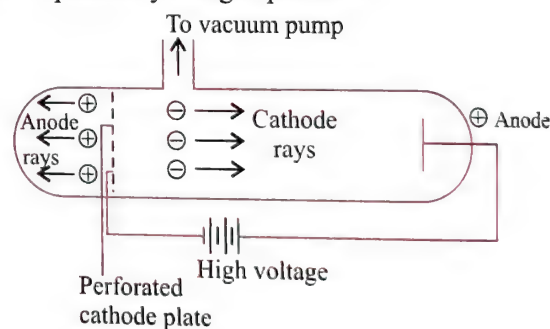


Fig. 4.4 Canal rays or anode rays

The characteristics of these positively charged particles are listed below:

- Anode rays travel in straight lines.
- Anode rays consist of material particles.
- Anode rays are deflected by electric field towards negatively charged plates. This indicates that they are positively charged.
- When a magnetic field is applied in the path of anode rays, they get deflected towards the direction expected for positive particles.
- Unlike cathode rays, the positively charged particles depend upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.
- The charge to mass ratio of the particles depends upon the nature of the gas taken in the discharge tube.

- g. Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

According to the above-mentioned characteristics, the charge to mass ratio (e/m) of the particles in the anode rays depends upon the nature of the gas in the discharge tube. e/m ratio is maximum when hydrogen gas in the discharge tube. This shows that positive ions formed from hydrogen are lightest. These positively charged particles are called protons. The charge to mass ratio for protons is 9.58×10^4 C/g. The charge on protons has the same magnitude as that of electrons but of opposite sign, i.e., 1.6022×10^{-19} C. From these two values, the mass of proton can be calculated and it is found to be 1.67×10^{-24} g or 1.673×10^{-27} kg. The mass of proton is same as the mass of a hydrogen atom, and it is about 1837 times the mass of an electron.

From the above observation it follows that a proton is a fundamental particle of atom carrying one unit positive charge and having mass nearly equal to the mass of an atom of hydrogen.

Note: 1. Cathode rays originate from the cathode. Anode rays do not originate from the anode.

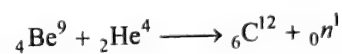
2. The cathode rays are ejected from cathode at right angles to its surface irrespective of the position of the anode.

3. Even if there is only one residual gas in a discharge tube, the different anode ray particles may have different specific charge (e/m). This is because different atoms of the gas may lose different number of electrons. However, most of the gas atoms lose only one electron. In this case e/m of different anode ray particles will be integral multiple of the lowest possible value.

4.5.1 DISCOVERY OF NEUTRON

The mass of an atom is mainly concentrated in its nucleus. The nucleus contains not only protons but also another type of particles called neutrons. These particles were discovered by

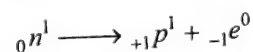
James Chadwick in 1932. He bombarded a thin foil of beryllium with fast-moving α -particles and observed that electrically neutral particles having a mass slightly greater than that of protons were emitted. These particles have very high penetrating power.



These neutral particles were found to have mass of 1.675×10^{-27} kg and were named neutrons and denoted by ${}_0n^1$. A neutron is a fundamental particle of atom present in the nuclei of all atoms except hydrogen or protium.

It is assumed that a neutron is a result of joining together an electron and a proton.

Being unstable, a neutron decays as follows:



Its half-life is 20 minutes.

4.6 OTHER PARTICLES OF ATOM

- Positron:** It was discovered by C.D. Anderson in 1932. It bears a unit positive charge, and its mass is equal to that of an electron. Thus, its mass is regarded as negligible. It merges with an electron and emits electromagnetic radiations. It is denoted by ${}_{+1}e^0$.
- Meson (π):** In 1935, Yukawa discovered this particle. Different types of meson particles can be found in an atom. These are called the meson family.
- Neutrino (${}_0e^0$):** Pauling discovered this particle in 1927. It does not bear any charge, i.e., it is an electroneutral particle.
- Antiproton:** Segre discovered this particle in 1956. It bears a unit negative charge, and its mass is equal to that of a proton.

The properties of the fundamental particles of atoms are summarised in Table 4.1.

Table 4.1 Some important subatomic particles

S.No.	Particles	Nature	Charge	Mass
1.	Electron (${}_1e^0$); discovered by J.J. Thomson	Negatively charged particle	-1.6022×10^{-19} C or -4.8×10^{-10} esu	0.00054 amu or 9.1×10^{-31} kg
2.	Proton (${}_1H^1$); discovered by Goldstein	Hydrogen nucleus	$+1.6022 \times 10^{-19}$ C or $+4.8 \times 10^{-10}$ esu	1.00727 amu or 1.673×10^{-27} kg
3.	Neutron (${}_0n^1$); discovered by Chadwick	Neutral particle	Zero charge	1.00867 amu or 1.675×10^{-27} kg
4.	Positron (${}_{+1}e^0$); discovered by Anderson		One unit positive charge	0.000549 amu or 9.1×10^{-31} kg
5.	Neutrino and antineutrino (${}_0e^0$); discovered by Fermi		Zero charge	0.00002 amu
6.	Meson (π) a. Positively, negatively charged meson; discovered by Yukawa b. Neutral meson; discovered by Kemmer	Positive (π^+) Neutral (π^0) Negative (π^-)	Positive charge No charge Negative charge	0.16107 amu

4.7 Radioactivity

The discovery of cathode rays and anode rays showed that Dalton's indivisible atom is composed of subatomic particles carrying positive and negative charges. This was further supported by the phenomenon of radioactivity discovered by Henry Becquerel in 1896. He observed that there are certain elements which emit radiations on their own and named this phenomenon as radioactivity and the elements as radioactive elements. This field was further developed by Marie Curie, Pierre Curie, Rutherford, and Frederick Soddy. It was observed that when a radioactive sample such as uranium was placed in a lead block and allowed the emitted rays from it to pass through strong electric and magnetic fields, the radiation resolved into three directions (Fig. 4.5)

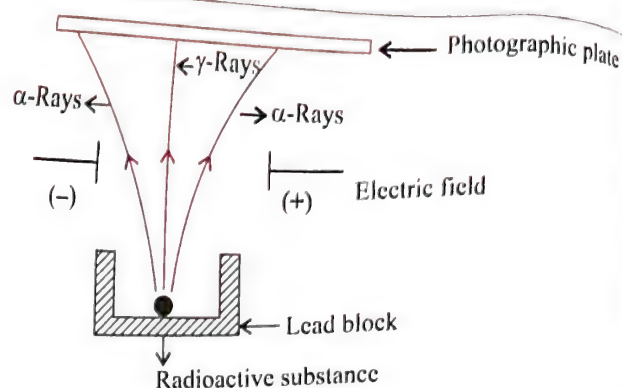


Fig. 4.5 Radioactive rays

- a. The rays which deflected slightly towards the negative plate were named as α -rays.

Table 4.2 Characteristics of α -, β -, and γ -rays

Property	α -Rays	β -Rays	γ -Rays
1. Mass	6.67×10^{-27} kg or 4 amu	9.11×10^{-31} kg	Negligible
2. Charge	+2 unit	-1 unit	0
3. Identity	Helium nuclei (He^{2+})	Electrons	High-energy radiations
4. Velocity	1/10th of the velocity of light	Nearly same as that of light	Same as that of light
5. Effect of electric field	Deflect towards negative plate	Deflect towards positive plate	No deflection
6. Penetrating power	Small of α -rays	Large, 100 times that of α -rays	Very large, 10000 times

- b. The rays which deflected towards the positive plate were named as β -rays.

- c. The rays which remained undeflected were named as γ -rays.

Rutherford found that α -rays consist of high energy particles carrying two units of positive charge and four units of atomic mass. He concluded that α -particles are helium nuclei because α -particles combined with two electrons to yield helium gas. β -rays are negatively charged particles similar to electrons. γ -rays are high-energy radiations like X-rays, are neutral in nature, and do not consist of particles. As regards penetrating power, α -particles have the least power, followed by β -rays (100 times that of α -particles) and γ -rays (1000 times that of α -particles).

4.8 ATOMIC MODELS

After the discovery of subatomic particles namely proton and electron, Dalton's atom was no more indivisible. It was suggested that an atom consisted of subatomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distribution of these charged particles in an atom. J.J. Thomson, in 1898, was the first to propose a detailed model of atom.

4.9 THOMSON MODEL

In 1898, J.J. Thomson proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. Electrons are embedded into it more or less uniformly to give the most stable electrostatic arrangement (Fig. 4.6). This model of atom is known as **plum pudding model** or **raisin pudding model** or **watermelon model**. This model can be visualised as pudding or watermelon of positive charges with plums or seeds (electrons) embedded into it.

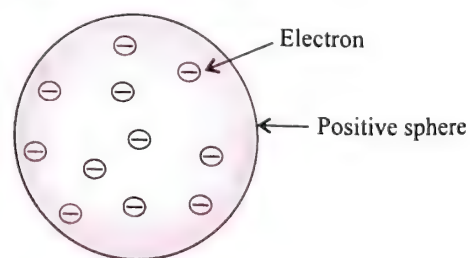


Fig. 4.6 Thomson's model of atom

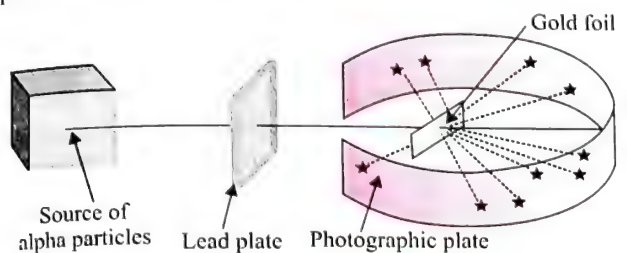
This model assumed that the mass of an atom is uniformly distributed over the atom.

This model was able to explain the electrical neutrality of atoms but failed to explain the results of later experiments such as Rutherford's famous α -particle scattering experiment. Thomson

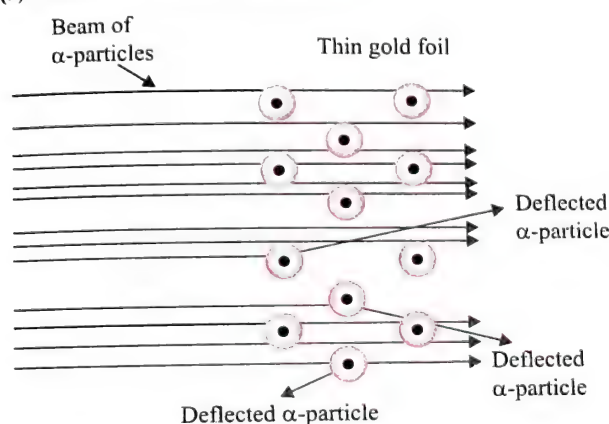
was awarded Nobel Prize for physics in 1906 for his theoretical and experimental investigations on the conduction of electricity in gases.

4.10 RUTHERFORD'S NUCLEAR MODEL

In 1911, British physicist Ernest Rutherford and two eminent experimenters Geiger and Marsden bombarded a very thin gold foil (thickness ~ 100 nm) with a stream of high energy α -particles. Rutherford's famous α -particle scattering experiment is represented in Fig. 4.7(a) and (b).



(a) Rutherford's scattering experiment



(b) Schematic molecular view of gold foil

Fig. 4.7 Schematic view of Rutherford's scattering experiment. When a beam of alpha (a) particles is shot at a thin gold foil, most of them pass through without much effect. Some, however, are deflected

The stream of α -particles obtained from a radioactive source passed through a slit in a lead plate was directed at a thin foil of gold metal. A circular fluorescent screen coated with zinc sulphide (ZnS) was placed around the foil to detect the deflection suffered by α -particles. Whenever a α -particle struck the screen, a tiny flash of light was produced at that point.

Rutherford observed that

- Most of the α -particles ($\sim 99\%$) passed through the gold foil undeflected.
- A small fraction of the α -particles was deflected by small angles.
- A very few α -particles (1 in 20,000) bounced back, that is, they were deflected by nearly 180° .

These results of scattering experiment were quite unexpected. These observations could not be explained by Thomson's model. According to the Thomson model of atom, the mass and charge

of an atom is uniformly distributed over the entire atom, and α -particles have enough energy to pass directly through such a uniform distribution of mass. It was expected that α -particles, while passing through the foil, would experience only a weak electric field and that the particles would slow down and suffer only a slight deflection by a small angle.

Rutherford, on the basis of his observation, drew the following conclusions regarding the structure of atom:

- Since most of the α -particles passed through the foil undeflected, it indicates that most of the space in an atom is empty.
- A few positively charged α -particles were deflected. The deflection must be due to an enormous repulsive force. This shows that the positive charge of an atom is not spread throughout the atom as Thomson had presumed. The positive charge is concentrated in a very small volume, which repelled and deflected the positively charged α -particles. Rutherford named this positive centre as nucleus.
- Rutherford calculated that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

Rutherford, on the basis of his observations and conclusions, proposed the nuclear model of atom.

4.10.1 MAIN POSTULATES OF THE MODEL

- Most of the mass and all the positive charge of an atom is concentrated in a very small region called nucleus. The size of the nucleus ($\sim 10^{-15}$) is extremely small as compared to the size of the atom ($\sim 10^{-10}$ m).
- The positive charge on the nucleus is due to protons.
- The nucleus is surrounded by electrons, which move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of the sun and the electrons play the role of revolving planets.
- Electrons and nucleus are held together by electrostatic forces of attraction.
- Total negative charge on the electrons is equal to the total positive charge on the nucleus. As a result, the atom on the whole is electrically neutral.
- Most of the space inside an atom is empty.
- The centrifugal force arising due to the high speed of an electron balances the coulombic force of attraction of the nucleus, and the electron remains in its path.

The Rutherford model of atom can be compared with the solar system. In an atom, electrons revolve around the nucleus in the same way as the planets revolve around the sun. Due to this comparison, revolving electrons are sometimes less called planetary electrons and Rutherford's nuclear model of atom is known as the planetary model of atom.

4.11 NUCLEAR STABILITY AND THE RATIO OF NEUTRONS AND PROTONS

The stability of a nucleus depends on the ratio of the number of neutrons (n) and protons (p) in it. A nucleus having n/p ratio approximately equal to 1 is found to be very stable. When the ratio of n and p is more than 1.5, the nucleus becomes unstable and radioactive. The atoms having $n = p$ are more stable, but with an increase in the atomic number, the number of neutrons goes on increasing in comparison to the number of protons. For example, the value of n/p is about 1 of atoms up to atomic number 20; hence, they are more stable. The value of n/p is between 1.5 and 1.6 for atoms having atomic number above 83; hence, they are radioactive. For example.

$$\text{In } {}_{20}\text{C}^{40}; \quad \frac{n}{p} = \frac{20}{20} = 1; \text{ the nucleus is stable.}$$

$$\text{In } {}_{92}\text{U}^{235}; \quad \frac{n}{p} = \frac{143}{92} = 1.55; \text{ the nucleus is unstable and;}$$

the atom is radioactive.

4.12 ATOMIC NUMBER

In 1913, H.G.J. Moseley carried out an experiment to find out the positive charge on the nucleus of an atom. He calculated the charge on the nucleus from the frequencies or wavelengths of the X-rays emitted by different elements. The number of unit positive charges on the nucleus of an atom of the element is called the atomic number of the element. The presence of positive charge on the nucleus is due to the protons in the nucleus, and each proton carries one unit positive charge. Therefore, the atomic number of an element is equal to the number of protons in the nucleus of its atom. As established earlier, the charge on protons is equal but opposite to that of electrons. Hence, the atomic number is also equal to the number of electrons in an atom of the element. The atomic number is denoted by the letter Z . Thus we have

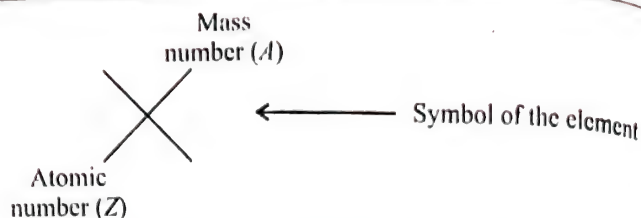
$$\begin{aligned} \text{Atomic number (Z)} &= \text{Number of protons in the} \\ &\quad \text{nucleus of an atom} \\ &= \text{Number of electrons in} \\ &\quad \text{a neutral atom} \end{aligned}$$

4.13 MASS NUMBER

The mass of an atom is mainly concentrated in the nucleus. As discussed earlier, protons and neutrons present in the nucleus are collectively known as nucleons. Thus, it follows that the mass of an atom is mainly due to protons and neutrons. It is generally represented by the letter A .

$$\begin{aligned} \text{Mass number (A)} &= \text{Number of protons} \\ &\quad + \text{Number of neutrons} \\ &= \text{Number of nucleons} \end{aligned}$$

The mass number and atomic number of an element are generally represented as shown below:



4.14 ISOTOPES, ISOBARS, ISOTONES, ISOELECTRONIC IONS

a. Isotopes: All atoms of a particular element have the same number of protons in their nuclei; however, the number of neutrons may be different. Such atoms have the same atomic number but different mass numbers and are known as isotopes of the element. Thus, atoms of the same element having the same atomic number but different atomic mass are called isotopes. For example, carbon has three isotopes represented by ${}_6\text{C}^{12}$, ${}_6\text{C}^{13}$, and ${}_6\text{C}^{14}$. All of them have the same atomic number, i.e. 6; however, their atomic mass are 12, 13, and 14, respectively. Similarly, hydrogen has three isotopes: protium (H), deuterium (D), and tritium (T). All of them have atomic number 1; their mass numbers are 1, 2, and 3, respectively.

b. Isobars: The atoms of different elements which have the same atomic mass number are called isobars. Isobars have different number of protons as well as neutrons, but the sum of protons and neutrons is same. For example,

Atomic mass of three elements ${}_{18}\text{Ar}^{40}$, ${}_{19}\text{K}^{40}$, ${}_{20}\text{Ca}^{40}$ is

	${}_{18}\text{Ar}^{40}$	${}_{19}\text{K}^{40}$	${}_{20}\text{Ca}^{40}$
Proton	18	19	20
Neutron	22	21	20

Similarly, ${}_6\text{C}^{14}$ and ${}_7\text{N}^{14}$ are isobars.

c. Isotones: Some atoms of different elements contain the same number of neutrons. Such atoms are known as isotones. Thus, isotones may be defined as atoms of different elements having the same number of neutrons. For example,

	${}_{14}\text{Si}^{30}$	${}_{15}\text{P}^{31}$	${}_{16}\text{S}^{32}$
Proton	14	15	16
Neutron	16	16	16

All three atoms have the same number of neutrons.

d. Ions: Atoms are neutral species containing an equal number of positive charges (protons) and negative charges (electrons). When an atom loses electron, it is converted into a cation. It has excess of positive charge equal to the number of electrons lost. It is converted into an anion on gaining electron. In this case, the atom acquires negative charge equal to the number of electrons gained. For example,

	${}_{11}\text{Na}^{\oplus}$	${}_{12}\text{Mg}^{2+}$	${}_{13}\text{Al}^{3+}$
Proton	11	12	13
Neutron	10	10	10

e. Isoelectronic ions: The ions of different elements may contain the same number of electrons. These ions are known as isoelectronic ions. Thus, the chemical species in which

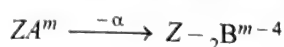
the number of electrons is same are called isoelectronic species. For example,

	Li^{\oplus}	Be^{2+}	B^{3+}
Number of electrons	2	2	2

In all the three ions, the number of electrons is same; hence, they are isoelectronic.

f. Isodiaphers: Atoms having the same difference of neutrons and protons, i.e., $(n - p)$, or the same isotopic numbers are called isodiaphers.

The nuclides and their decay products after an emission are also called isodiaphers. For example,



g. Isosters: Molecules having the same number of atoms and the same number of electrons are called isosters. For example, CO_2 and N_2O are isosters.

ILLUSTRATION 4.3

Calculate the number of protons, neutrons and electrons in ${}_{35}\text{Br}^{80}$ in the following species:

Sol. $Z = 35$, $A = 80$, species is neutral.

\therefore Number of protons = number of electrons = $Z = 35$.

Number of neutrons = $80 - 35 = 45$

ILLUSTRATION 4.4

Give an isobar, isotone, and isotope of ${}_6\text{C}^{14}$.

Sol. Isobar of ${}_6\text{C}^{14}$ is ${}_7\text{N}^{14}$.

Isotone of ${}_6\text{C}^{14}$ is ${}_8\text{O}^{16}$.

Isotope of ${}_6\text{C}^{14}$ is ${}_6\text{C}^{13}$.

ILLUSTRATION 4.5

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species

Sol. $Z = 16$, The element is sulphur (S)

Atomic mass number = number of protons + number of neutrons = $16 + 16 = 32$

Species is not neutral as the number of protons is not equal to electrons. It is negatively charged equal to excess electrons = $18 - 16 = 2$.

Symbol is ${}_{16}^{32}\text{S}^{2-}$

ILLUSTRATION 4.6

If the atomic weight of Zn is 70, and its atomic number is 30, then what will be the atomic weight of Zn^{2+} ?

Sol. In the formation of Zn^{2+} from Zn, two electrons are removed. The number of protons and neutrons remains unchanged; hence, the atomic weight of Zn^{2+} will be 70.

ILLUSTRATION 4.7

The mass numbers of three isotopes of an element are 10, 12, and 14 units. Their percentage abundance is 80, 15, and 5, respectively. What is the atomic weight of the element?

Sol. The percentage abundances of isotopes are 80, 15, and 5. Thus their ratio is 16 : 3 : 1.

Total of the ratio = $16 + 3 + 1 = 20$

Average weight = $\frac{\% \text{ abundance} \times \text{Atomic number}}{\text{Total of ratio}}$

\therefore Average weight = $\frac{10 \times 16 + 12 \times 3 + 14 \times 1}{20} = 10.5$

Thus, the average atomic weight is 10.5 unit.

ILLUSTRATION 4.8

I. The pair NH_3 and BH_3 is isoelectronic with

a. B_2H_6 b. C_2H_6 c. C_2H_4 d. CO_2

II. In Rutherford's scattering experiment, which of the following does not happen?

- Most of the α -rays pass through without deflection.
- A few α -particles pass through the nucleus.
- A few α -particles are deflected back.
- α -particles going near the nucleus are slightly deflected.

III. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because

- Alpha particles are much heavier than electron.
- Alpha particles are positively charged.
- Alpha particles move with high velocity.
- Most part of the atom is empty.

IV. Which of the following statements about proton is correct?

- Proton is the nucleus of deuterium.
- Proton is an α -particle.
- Proton is an ionised hydrogen molecule.
- Proton is ionised hydrogen.

V. Rutherford's experiment, which established the nuclear model of atom, used a beam of

- β -Particles, which impinged on a metal foil and got absorbed
- γ -Rays, which impinged on a metal foil and ejected electrons
- Helium atoms, which impinged on a metal foil and got scattered
- Helium nuclei, which impinged on a metal foil and got scattered

VI. Which of the following shows an increasing value of e/m ?

- $n < \alpha < p < e$
- $n < p < \alpha < e$
- $n < p < e < \alpha$
- $p < n < \alpha < e$

VII. From the α -particle scattering experiment, Rutherford concluded that

- α -Particles can come within a distance of the order of 10^{-14} m of the nucleus
- The radius of the nucleus is less than 10^{-14} m

- c. Scattering follows coulomb's law
 d. The positively charged parts of the atom move with extremely high velocities.

VIII. Which of the following statements regarding cathode rays is not correct?

- a. Cathode rays originate from the cathode
 b. The charge and mass of the particles constituting cathode rays depend upon the nature of the gas
 c. The charge and mass of the particles present does not depend upon the material of the cathode
 d. The charge/mass ratio of the particles is much greater than that of anode rays.

Sol.

- I. b. In the pair NH_3 and BH_3 , the atomic number is $7 + 3 + 5 + 3 = 18$. The atomic number is equal to the number of protons and the number of electrons. A C_2H_6 molecule has the atomic number 18, which is equal to that of NH_3 and BH_3 . Thus, C_2H_6 is isoelectronic with NH_3 and BH_3 .
 II. b. α -particles does not pass through the nucleus because the nucleus is heavy.
 III. d. Most part of the atoms is empty.
 IV. d. Proton is ionised hydrogen.
 V. d. Helium nuclei, which impinged on a metal foil and got scattered.
 VI. a. $n < \alpha < p < e$
 VII. (a, b, c)
 VIII. b. The charge and mass of the particles constituting cathode rays depend upon the nature of the gas.

ILLUSTRATION 4.9

Oxygen consists of isotopes O^{16} , O^{17} , and O^{18} , and carbon consists of isotopes C^{12} and C^{13} . How many types of CO_2 molecules can be formed? Also report their molecular weights.

Sol. Total number of molecules of $\text{CO}_2 = 12$

Types of molecules	Molecular weight
1. $\text{C}^{12}\text{O}^{16}\text{O}^{16}$	44
2. $\text{C}^{12}\text{O}^{17}\text{O}^{17}$	46
3. $\text{C}^{12}\text{O}^{18}\text{O}^{18}$	48
4. $\text{C}^{12}\text{O}^{16}\text{O}^{17}$	45
5. $\text{C}^{12}\text{O}^{16}\text{O}^{18}$	46
6. $\text{C}^{12}\text{O}^{17}\text{O}^{18}$	47

Similarly, six molecules with C^{13} isotopes can be found.

ILLUSTRATION 4.10

The atomic masses of two isotopes of O are 15.9936 and 17.0036. Calculate in each atom

- a. Number of neutrons b. Number of protons
 c. Number of electrons d. Mass number

Sol.

First isotope of O	Second isotope of O
--------------------	---------------------

Atomic mass	15.9936	17.0036
a. Number of neutrons	$16 - 8 = 8$	$17 - 8 = 9$
b. Number of protons	$16 - 8 = 8$	$17 - 9 = 8$
	(Mass number - Number of neutrons)	
c. Number of electrons	8	8
d. Mass number	16	17

ILLUSTRATION 4.11

Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron.

Sol. Let the percentage of isotope with atomic weight 10.01 be x .

So the percentage of isotope with atomic weight 11.01 will be $100 - x$.

$$\begin{aligned} \text{Average atomic weight} &= \frac{m_1x_1 + m_2x_2}{x_1 + x_2} \\ &= \frac{x \times 10.01 + (100 - x) \times 11.01}{100} \end{aligned}$$

$$10.81 = \frac{x \times 10.01 + (100 - x) \times 11.01}{100} = 20$$

$$\therefore \% \text{ of isotope with atomic weight } 10.01 = 20$$

$$\% \text{ of isotope with atomic weight } 11.01 = 100 - x = 80$$

ILLUSTRATION 4.12

What will be the difference in the mass number if the number of neutrons is halved and the number of electrons is doubled in ${}_8\text{O}^{16}$?

- a. 25% decrease b. 50% increase
 c. 150% increase d. No difference

Sol.

a. ${}_8\text{O}^{16}$ Initial weight-final weight

Protons	$8p$	\rightarrow	$8p$
Neutrons	$8n$	\rightarrow	$4n$
Weight	16	\rightarrow	12

Thus decrease in mass number = 25%

ILLUSTRATION 4.13

The mass of 1 mol of electrons is

- a. 0.55 mg b. 1.0008 g c. 1.000 g d. 0.184 g

Sol.

a. The number of electrons in one mole = Avogadro number
 $= 6.023 \times 10^{23}$

Mass of one electron = 9.1×10^{-28} g

Therefore, mass of 6.023×10^{23} electrons is
 $= 9.1 \times 10^{-26} \times 6.023 \times 10^{23} = 0.55$ mg

ILLUSTRATION 4.14

In two elements ${}_Z\text{A}^{M_1}$ and ${}_Z\text{B}^{M_2}$. $M_1 \neq M_2$ and $Z_1 \neq Z_2$ but

$M_1 - Z_1 = M_2 - Z_2$. These elements are

- a. Isotonic b. Isobaric c. Isotopic d. Isoprotonic

- Sol.** a. $M_1 = \text{Atomic weight}$ $Z_1 = \text{Atomic number}$
 In isobars $M_1 = M_2$ and in isotopes $Z_1 = Z_2$.
 In isotones (isoneutronic elements) $M_1 - Z_1 = M_2 - Z_2$

ILLUSTRATION 4.15

Two nuclides A and B are isoneutronic. Their mass numbers are 76 and 77, respectively. If the atomic number of A is 32, then the atomic number of B will be

- a. 33 b. 34 c. 32 d. 30

Sol. a.

${}_{32}\text{A}^{76}$		${}_p\text{B}^{77}$	
Protons	= 32	Protons + Neutrons	= 77
Protons + Neutrons	= 76	Neutrons	= 44
Neutrons	= 44	Protons	= 33

ILLUSTRATION 4.16

What is the percentage of deuterium in heavy water?

- a. 20% b. 80% c. 60% d. 40%

Sol. a. Deuterium in 20 parts of $\text{D}_2\text{O} = 4$ parts

$$\text{Deuterium in 100 parts of } \text{D}_2\text{O} = \frac{4}{20} \times 100 = 20\%$$

ILLUSTRATION 4.17

Which of the following pairs consists of molecules having the same mass number?

- a. H_2O and D_2O b. H_2O and HTO
 c. D_2O and HTO d. D_2O and HCl

Sol. c. Mass number of $\text{H}_2\text{O} = 18$

$$\text{Mass number of } \text{D}_2\text{O} = 20$$

$$\text{Mass number of } \text{HTO} = 20$$

$$\text{Mass number of } \text{HCl} = 36.5$$

ILLUSTRATION 4.18

The mass number of three isotopes of an element are 11, 12, and 13 units. Their percentage abundances 80, 15, and 5, respectively. What is the atomic weight of the element?

- a. 11.25 b. 20 c. 16 d. 10

Sol. a. 80 : 15 : 5

$$\text{Thus, the ratio is } 16 : 3 : 1.$$

$$\text{Total} = 16 + 3 + 1 = 20$$

$$\text{Average weight} = \frac{11 \times 16 + 12 \times 3 + 13 \times 1}{20} = 11.25$$

ILLUSTRATION 4.19

If two neutrons are added to an element X, then it will get converted to its

- a. Isotope b. Isotone
 c. Isobar d. None of the above

II. The isoelectronic pair of 32 electrons is

- a. BO_3^{3-} and CO_3^{2-} b. N_2 and CO
 c. PO_4^{3-} and CO_3^{2-} d. All of the above

III. Which of the following is a one-electron species?

- a. He b. N c. H_2 d. N_2

IV. The molecular weight of an oxide of nitrogen is 30. What is the number of electrons in it?

- a. 15 b. 30 c. 45 d. 20

V. A diapositive ion has 16 protons. What is the number of electrons in its tetrapositive ion?

- a. 16 b. 14 c. 12 d. 10

VI. If the atomic weights of C and Si are 12 and 28, respectively, then what is the ratio of the numbers of neutrons in them?

- a. 1 : 2 b. 2 : 3 c. 3 : 4 d. 3 : 7

Sol.

I. a. The numbers of neutrons are different in the isotopes of the same element.

II. a. BO_3^{3-} CO_3^{2-}
 $5 + 24 + 3 = 32$ $6 + 24 + 2 = 32$

III. c. There is only one electron in H_2^+ .

IV. a. The molecular weight of NO is 30. It will have 15 electrons.

V. c. X^{2+} has 16 protons, then
 in X, there are 16 protons and 16 electrons
 in X^{2+} , there are 16 protons and 14 electrons
 in X^{4+} , there are 16 protons and 12 electrons

VI. a. Number of neutrons in ${}_6\text{C}^{12} = 12 - 6 = 6$
 Number of neutrons in ${}_{14}\text{Si}^{28} = 28 - 14 = 14$

The ratio of the numbers of neutrons in C and Si is 6 : 14 or 3 : 7.

ILLUSTRATION 4.20

Calculate the density of fluorine nucleus supposing that the shape of the nucleus is spherical and its radius is 5×10^{-13} . (Mass of F = 19 amu)

Sol. Mass of the nucleus of F atom = $19 \times 1.66 \times 10^{-24}$ g
 (1 amu = 1.660×10^{-24} g)

$$\begin{aligned} \text{Volume of the nucleus of F atom} &= \frac{4}{3} \pi r^3 \\ &= \frac{4}{3} \times 3.14 (5 \times 10^{-13})^3 \\ &= 525 \times 10^{-39} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Density of the nucleus of F atom} &= \frac{\text{Mass}}{\text{Volume}} \\ &= \frac{19 \times 1.66 \times 10^{-24} \text{ g}}{525 \times 10^{-39} \text{ cm}^3} \\ &= 6.0 \times 10^{13} \text{ g cm}^{-3} \end{aligned}$$

ILLUSTRATION 4.21

Calculate:

- The number of electrons which will together weigh 1 g.
- The mass of 1 mol of electrons.
- The charge of 1 mol of electrons.

Sol.

- 9.1×10^{-28} g is the mass of 1 electron.

$$1 \text{ g is the mass of } \frac{1 \times 1}{9.1 \times 10^{-28}} = 1.09 \times 10^{27} \text{ electrons}$$

- 1 mol of electrons = 6.02×10^{23}

$$\text{Mass of 1 electron} = 9.1 \times 10^{-28} \text{ g}$$

$$\begin{aligned} \text{Mass of } 6.02 \times 10^{23} \text{ electrons} \\ = 6.02 \times 10^{23} \times 9.1 \times 10^{-28} \\ = 5.478 \times 10^{-4} \text{ g} \end{aligned}$$

- 1 mol of electrons = 6.02×10^{23} electrons

$$\text{Charge of electron} = 1.60 \times 10^{-19} \text{ C}$$

$$\begin{aligned} \text{Charge of } 6.02 \times 10^{23} \text{ electrons} \\ = 1.60 \times 10^{-19} \times 6.02 \times 10^{23} \text{ C} \\ = 9.632 \times 10^4 \text{ C} \end{aligned}$$

ILLUSTRATION 4.22

Nitrogen atom has atomic number 7 and oxygen has atomic number 8. Calculate the total number of electrons in nitrate ion.

Sol. Formula of nitrate ion = NO_3^-

$$\begin{aligned} \text{Number of electrons in } \text{NO}_3^- &= \text{Electrons in N} \\ &\quad + 3 \times \text{electrons in O} \\ &\quad + 1 \text{ (due to negative charge)} \\ &= 7 + 3 \times 8 + 1 = 32 \end{aligned}$$

4.15 DRAWBACKS OF RUTHERFORD MODEL

The Rutherford nuclear model of atom is like a small-scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. The similarity between the solar system and the nuclear model suggests that electrons should move around the nucleus in well-defined orbits. However, when a body moves in an orbit, it undergoes acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated emit radiation. (This feature does not exist for planets since they are uncharged.) Therefore, an electron in an orbit will emit radiation; the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink, due to which the electron would ultimately plunge into the nucleus, as shown in Fig. 4.8.

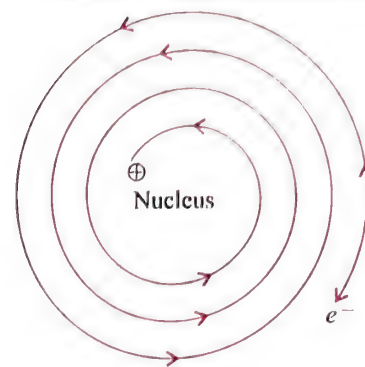


Fig. 4.8 An electron emitting energy and plunging into nucleus

Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. This means an atom should collapse, but this does not happen. Thus, *Rutherford's model failed to explain the stability of an atom.*

Another serious drawback of the Rutherford model is that it does not explain the electronic structure of atoms, i.e., how electrons are distributed around the nucleus and what are the energies of these electrons. *Rutherford's model also failed to explain the existence of certain definite lines in the hydrogen spectrum.* If an electron moving around the nucleus continuously emits energy, then the atomic spectrum must be continuous, i.e., the spectrum should not have lines of definite frequency. However, the atomic spectrum is actually not continuous, and it possesses so many lines of definite frequency.

4.16 NATURE OF ELECTROMAGNETIC RADIATIONS

4.16.1 WAVE NATURE OF ELECTROMAGNETIC RADIATIONS

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between charged bodies and the behaviour of electrical and magnetic fields on the macroscopic level. He suggested that when an electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called *electromagnetic waves* or *electromagnetic radiations*.

Light is the form of radiation known from early days, and speculations about its nature date back to ancient times. In earlier days, light was supposed to be made of particles (corpuscles). Newton's corpuscular theory could successfully explain the phenomena of refraction and reflection but failed to explain the phenomena of diffraction and interference. Therefore, the corpuscular theory was discarded and was replaced by Maxwell's wave theory of light. According to this theory, light is transmitted in the form of electromagnetic waves. These waves are associated with oscillating electric and magnetic fields. The important properties of electromagnetic waves are listed below:

- The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other. Both are perpendicular to the direction of propagation of

the wave. A simplified picture of an electromagnetic wave is shown in Fig. 4.9.

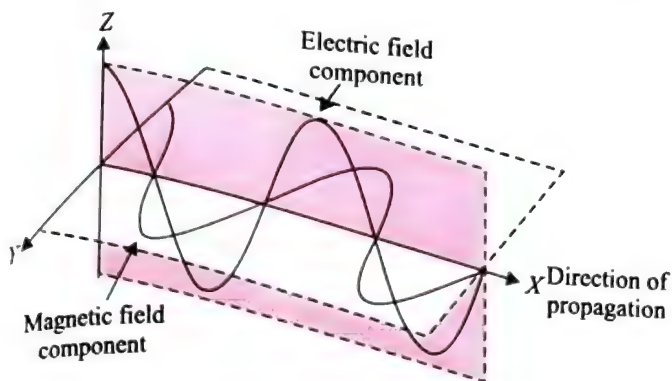


Fig. 4.9 The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed, and amplitude, but they vibrate in two mutually perpendicular planes

b. Unlike sound waves or water waves, electromagnetic waves do not require a medium and can move in vacuum.

Different kinds of units are used to characterise electromagnetic radiations.

i. **Wavelength:** It is defined as the distance between two neighbouring crests or troughs of a wave as shown in Fig. 4.10. Wavelength is represented by the Greek letter λ (lambda) and is generally measured in angstrom (\AA) or nanometre (nm).

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ nm} = 10^{-9} \text{ m}$$

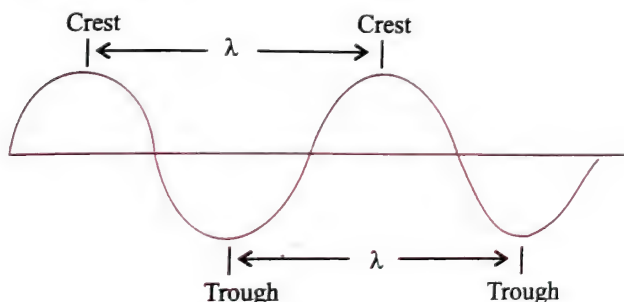


Fig. 4.10 Propagation of wave motion

ii. **Frequency:** The number of waves which pass through a particular point in one second is defined as the frequency of wave motion. It is represented by the Greek letter ν (nu). The SI unit for frequency (ν) is hertz (Hz) after Heinrich Hertz.

Cycles per second (cps) or hertz (Hz)

$$1 \text{ cps} = 1 \text{ Hz}$$

$$1 \text{ kHz} = 10^3 \text{ Hz}$$

$$1 \text{ MHz} = 10^6 \text{ Hz}$$

iii. **Velocity:** The distance travelled by a wave in one second is called the velocity of the wave. It is represented by the letter c . The frequency (ν), wavelength (λ), and velocity of light (c) are related by the equation

$$c = \nu \lambda$$

In vacuum, all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., $3.0 \times 10^8 \text{ m s}^{-1}$. This is called the speed of light.

iv. **Wavenumber:** It may be defined as the number of wavelengths per unit length. It is equal to the inverse of wavelength. It is denoted by $\bar{\nu}$. Its unit is the reciprocal of the wavelength unit, i.e., m^{-1} .

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

v. **Amplitude:** It is the height of a crest or depth of a trough of a wave. It is denoted by the letter A . The amplitude of a wave determines the intensity of radiation.

vi. **Electromagnetic spectrum:** It is now well established that there are many types of electromagnetic radiations which differ from one another in wavelength or frequency. These constitute *electromagnetic spectrum* (Fig. 4.11). Different regions of the spectrum are identified by different names. Some examples are follows: radio frequency region around 10^6 Hz , used for broadcasting; microwave region around 10^{10} Hz , used for radar; infrared region around 10^{13} Hz , used for heating; ultraviolet region around 10^{16} Hz , a component of sun's radiation. The small portion around 10^{15} Hz is what is ordinarily called *visible light*. It is only this part which our eyes can see (or detect). Special instruments are required to detect invisible radiation.

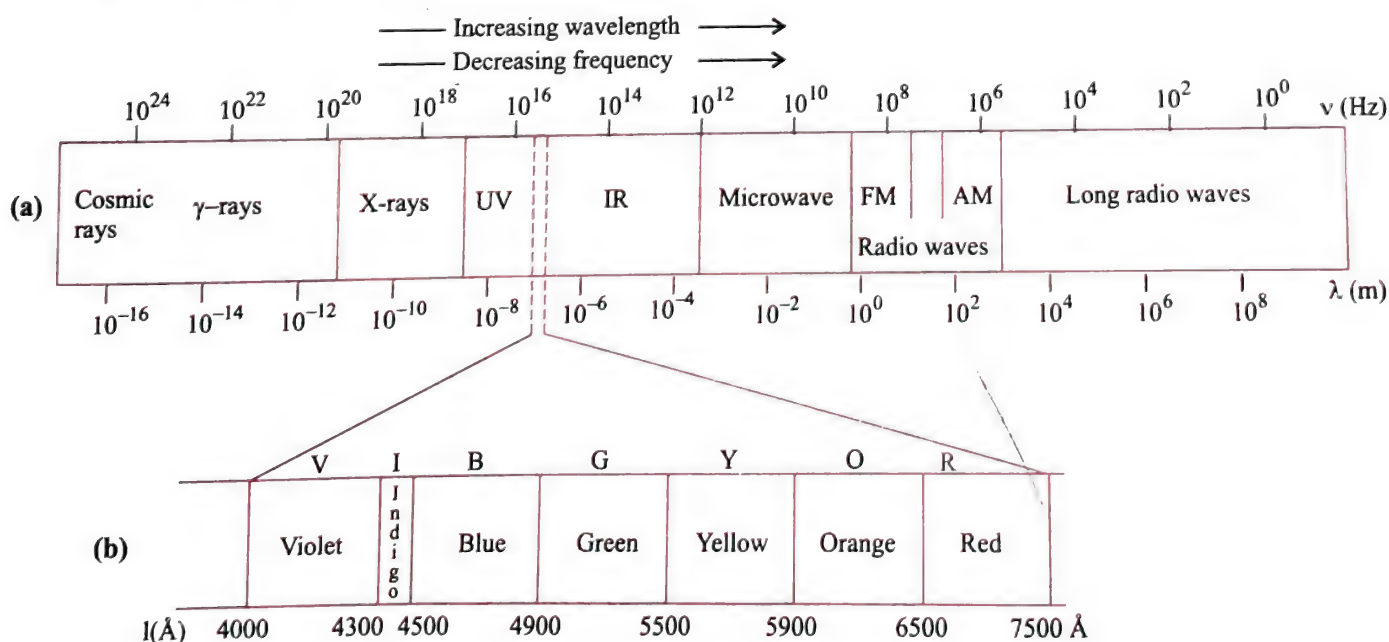


Fig. 4.11 (a) The spectrum of electromagnetic radiation and (b) the visible spectrum

Various types of electromagnetic radiations have different energies and are being used for different applications as listed in Table 4.3.

Table 4.3 Some applications of electromagnetic waves

Name	Frequency (Hz)	Wavelength (m)	Uses
Gamma rays	10^{20} to 10^{21}	10^{-12}	Cancer treatment
X-rays	10^{17} to 10^{21}	10^{-10}	Medical 'pictures', material testing
Ultraviolet	10^{15} to 10^{16}	10^{-7}	Germicidal lamps
Visible	10^{13} to 10^{14}	10^{-6}	Illumination
Infrared	10^{12} to 10^{13}	10^{-4}	Heating
Microwave	10^9 to 10^{11}	10^{-2}	Cooking radar
Radio frequency	10^5 to 10^8	10^2	Signal transmission

4.17 MOSELEY'S EXPERIMENT

Roentgen obtained a new type of electromagnetic radiation when a target material (anti-cathode) was placed in the path of cathode rays. These electromagnetic radiations were called X-rays.

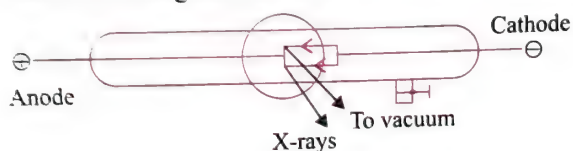


Fig. 4.12

By using different X-ray tubes provided with anti-cathodes of different materials, Moseley was able to take the spectrum of X-rays in each case. It was observed that the wavelengths of X-rays were the characteristic of each element. The characteristic X-ray spectrum consists of discrete spectral lines which can be grouped into K-series, L-series, M-series, etc.

4.17.1 ANALYSIS OF THE RESULT

It was suggested by Moseley that the fast-moving cathode rays were able to remove electrons from the inner orbits (i.e., K, L, M, etc.) of an atom of anti-cathode due to collision. This creates vacancy in the inner shells. Under the influence of nuclear charges electrons from higher shells fall in those shells.

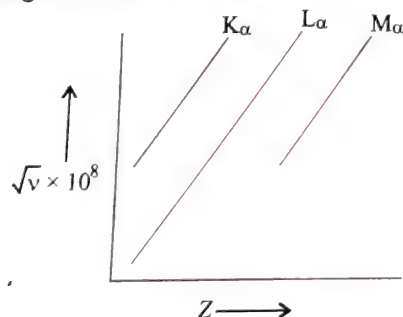


Fig. 4.13

Moseley showed that the square root of the frequency (\sqrt{v}) of a spectral line is strictly related to the nuclear charge (Z) if the excitation potential is fixed.

When a graph is plotted between $\sqrt{v} \times 10^8$ and the atomic number (Z), a straight line is obtained.

The results obtained led to the suggestion that \sqrt{v} must be directly proportional to the atomic number of an element (Z).

$$\sqrt{v} \propto Z$$

To give accurate results, Moseley modified this equation as

$$\sqrt{v} \propto (Z - b)$$

where b is a constant and is known as the screening constant. For K_α and K_β lines, $b = 1$.

$$\text{Hence, } \sqrt{v} \propto a(Z - 1) \quad \dots(i)$$

where a is the proportionality constant.

This equation is very useful for the calculation of Z if the frequency of K_α and K_β lines are known.

Hence, on combining the result, we get the square root of frequency as $\sqrt{v} = a(Z - b)$

ILLUSTRATION 4.23

The Vividh Bharti station of All India Radio, Delhi, broadcasts on a frequency of 1.368 kHz (kilohertz). Calculate the wavelength of the electro-magnetic radiation emitted by transmitter. Which part of electromagnetic spectrum does it belong to?

$$\begin{aligned} \text{Sol. } \lambda &= \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{1368 \text{ kHz}} \\ &= \frac{3.00 \times 10^8 \text{ ms}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} \\ &= 219.3 \text{ m} \end{aligned}$$

This is a characteristic radiowave wavelength.

ILLUSTRATION 4.24

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelength in frequencies (Hz). (1 nm = 10^{-9} m).

Sol. Frequency of violet light is:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.50 \times 10^{14} \text{ Hz}$$

Frequency of red light is:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{750 \times 10^{-9} \text{ m}} = 4.00 \times 10^{14} \text{ Hz}$$

The range of visible spectrum is from 4.0×10^{14} to 7.5×10^{14} Hz in terms of frequency units.

ILLUSTRATION 4.25

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 \AA .

Sol.

a. Calculation of wave number ($\bar{\nu}$)

$$\lambda = 5800 \text{ \AA} = 5800 \times 10^{-8} \text{ cm}$$

$$= 5800 \times 10^{-10} \text{ m}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10} \text{ m}}$$

$$= 1.724 \times 10^6 \text{ m}^{-1}$$

$$= 1.724 \times 10^4 \text{ cm}^{-1}$$

b. Calculation of the frequency (ν)

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{5800 \times 10^{-10} \text{ m}}$$

$$= 5.172 \times 10^{14} \text{ s}^{-1}$$

ILLUSTRATION 4.26

Calculate the wavelength of an ultraviolet wave, if its frequency is 12×10^{16} cycles per second and $c = 3 \times 10^8 \text{ m s}^{-1}$?

Sol. Velocity of radiation $= 3 \times 10^8 \text{ m s}^{-1}$

Frequency of radiation $= 12 \times 10^{16} \text{ Hz}$

$$\therefore \text{Wavelength } (\lambda) = \frac{c}{\nu} = \frac{3 \times 10^8}{12 \times 10^{16}} = 0.25 \times 10^{-8} \text{ m}$$

$$\text{or } \lambda = 2.5 \times 10^{-9} \text{ m}$$

ILLUSTRATION 4.27

I. A photon in X region is more energetic than in the visible region; X is

- a. IR rays b. UV rays
c. Microwaves d. Radiowaves

II. The coloured radiation with lowest energy is

- a. Red b. Blue
c. Green d. Yellow

III. Moseley's equation for the determination of wavelength of X-rays is (ν = frequency of wave, Z = nuclear charge, a and b are constants)

a. $\sqrt{\nu} = (Z - ab)$ b. $\nu = a(Z - b)$

c. $\sqrt{\nu} = a(Z - b)$ d. $\nu = (Z - ab)$

Sol.

I. b. UV

II. a. Red

III. c. $\sqrt{\nu} = a(Z - b)$

ILLUSTRATION 4.28

I. Of the following, the radiation having the maximum wavelength is

- a. UV rays b. Radiowaves c. X-rays d. IR rays

II. Out of the following the radiation with lowest frequency is

- a. IR rays b. γ -Rays
c. Cosmic rays d. Microwaves

III. Which of the following statements about the electromagnetic spectrum is not correct?

- a. IR radiations have larger wavelength than cosmic rays.
b. The frequency of microwaves is less than that of UV rays.
c. X-rays have larger wavenumber than microwaves.
d. The velocity of X-rays is more than that of microwaves.

Sol.

I. b. Radiowaves

II. d. Microwaves

III. d. The velocity of X-rays is more than that of microwaves.

ILLUSTRATION 4.29

The mass-charge ratio for A^+ ion is $1.97 \times 10^{-7} \text{ kg C}^{-1}$. Calculate the mass of A atom.

Sol. Given $\frac{m}{e} = 1.97 \times 10^{-7}$ (since $e = 1.602 \times 10^{-19} \text{ C}$)

$$\therefore m = 1.97 \times 10^{-7} \times 1.602 \times 10^{-19} \text{ kg}$$

$$m = 3.16 \times 10^{-26} \text{ kg}$$

ILLUSTRATION 4.30

I. Atomic radius is of the order of 10^{-8} cm and nuclear radius is of the order of 10^{-13} cm . What fraction of an atom is occupied by nucleus?

II. Nuclear radius is of the order of 10^{-13} cm , while atomic radius is of the order of 10^{-8} cm . Assuming the nucleus and the atom to be spherical, what fraction of the atomic volume is occupied by the nucleus?

III. The ratio e/m , i.e., specific charge, for a cathode ray

- a. Has the smallest value when the discharge tube is filled with H_2 .
b. Is constant.
c. Varies with the atomic number of gas in the discharge tube.
d. Varies with the atomic number of an element forming the cathode.

Sol.

I. Volume of nucleus $= \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (10^{-13})^3 \text{ cm}^3$

Volume of atom $= \frac{4}{3} \pi (10^{-8})^3 \text{ cm}^3$

$$\frac{V_{\text{Nucleus}}}{V_{\text{Atom}}} = \frac{10^{-39}}{10^{-24}} = 10^{-15}$$

$$\frac{\text{Nuclear volume}}{\text{Atomic volume}} = \frac{\frac{4}{3}\pi(10^{-13})^3}{\frac{4}{3}\pi(10^{-8})^3} = 10^{-15}$$

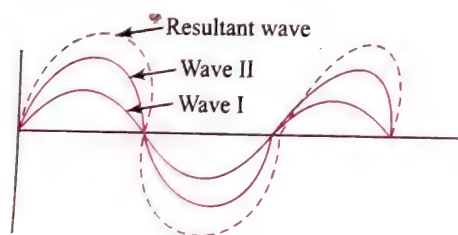
III. The ratio is constant.

4.18 PARTICLE NATURE OF ELECTROMAGNETIC RADIATIONS: PLANCK'S QUANTUM THEORY

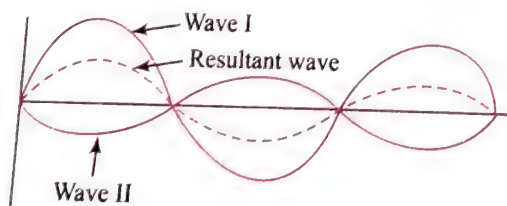
The wave theory of radiation could successfully explain the phenomena of reflection, refraction, dispersion, diffraction and interference.

- Note:**
- Reflection:** It is reflecting of wave after striking on some surface.
 - Refraction:** It is bending of wave when it passes from one medium to another.
 - Dispersion:** It is splitting of group of waves into different waves when it passes through a prism.
 - Diffraction:** It is the bending of wave around an obstacle or corner.
 - Interference:** It is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the vector sum of disturbances at that point resulting from each interfering wave.

When two waves of same phases overlap each other it is called **constructive interference**. When two waves of opposite phases overlap it is called **destructive interference**.



Constructive interference due to waves in same phases



Destructive interference due to waves in opposite phase

However, following are some of the observations which could not be explained with the help of the electromagnetic theory:

- Black body radiation, i.e., the nature of emission of radiation from hot bodies.
- Photoelectric effect, i.e., the ejection of electrons from metal, surface when radiation strikes it.

c. The variation of heat capacity of solids as a function of temperature.

d. Line spectra of atoms with special reference to hydrogen.

4.19 BLACK BODY RADIATION

In 1900, **Max Planck** was the first to give a concrete explanation for the phenomenon of black body radiation. According to the Max Planck theory, an ideal body is a perfect absorber and perfect emitter of radiation and is called a **black body**. The radiation emitted by such a body is called **black body radiation**. When such a body is heated, it emits radiation over a wide range of wavelengths.

For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. On heating further, the radiation emitted becomes white and then blue as the temperature becomes very high. In terms of frequency, it means that the radiation emitted goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies in the lower frequency region while the blue colour belongs to the higher frequency region of the electromagnetic spectrum. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature. At a given temperature, the intensity of radiation emitted increases with a decrease in wavelength, reaches a maximum value at a given wavelength, and then starts decreasing with further decrease in wavelength, as shown in Fig. 4.14.

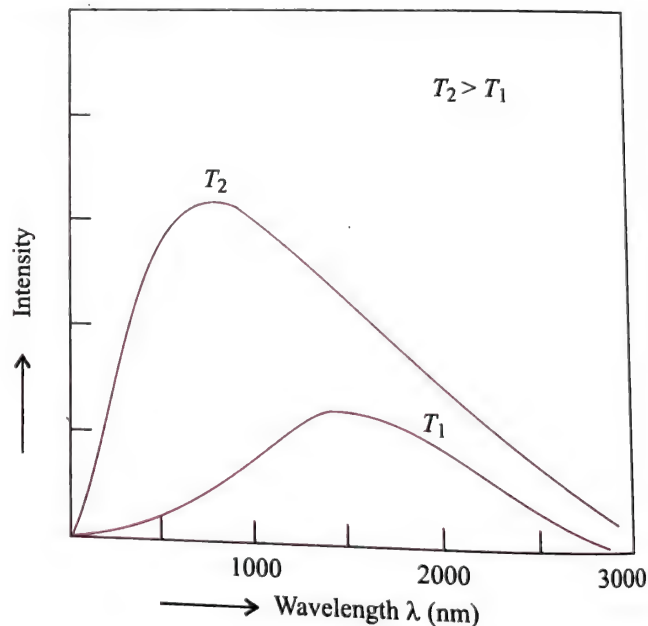


Fig. 4.14 Wavelength-intensity relationship

The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. In 1900, Max Planck provided an explanation for this behaviour. He said that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in an arbitrary amount or in a continuous manner (Fig. 4.15) as was believed till then. Planck gave the name **quantum** to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy of a quantum of radiation is proportional to its frequency and is expressed as

$$E = h\nu \text{ or } E = \frac{hc}{\lambda} = hc\bar{\nu}$$

where ν = frequency

$\bar{\nu}$ = wavenumber

λ = wavelength

c = velocity

The proportionality constant, h , is known as the Planck constant and has the value 6.626×10^{-34} J s. According to Planck's theory, energy is always emitted in integral multiples of $h\nu$, for example $h\nu$, $2h\nu$, $3h\nu$, etc. Planck, however, could not explain why energies should be quantised in this manner. However, with this assumption, Planck could explain the distribution of intensity in radiation from a black body as a function of frequency or wavelength at different temperatures.

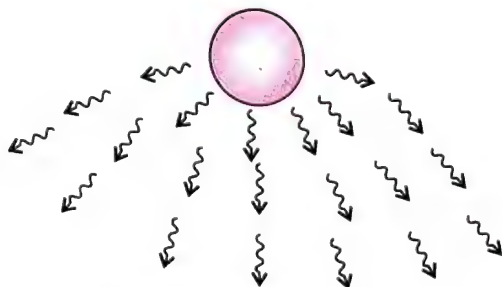


Fig. 4.15 Heated iron ball emitting energy in discrete quantities

The assumptions of Planck's theory are listed below:

- Each radiation is always associated with a definite amount of energy and is known as radiant energy.
- Radiant energy is emitted or absorbed discontinuously in the form of small packets of energy called quanta.

Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is called *photon*.

- The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation.

$$E \propto \nu$$

$$\text{or } E = h\nu = \frac{hc}{\lambda}$$

- The energy emitted or absorbed by a body is always an integral multiple of quanta, i.e., $E = nh\nu$, where $n = 1, 2, 3, \dots$ etc.

ILLUSTRATION 4.31

Calculate and compare the energies of two radiations, one with a wavelength of 300 nm and the other with 600 nm.

Sol. Energy of radiation (E) = $h\nu = \frac{hc}{\lambda}$

$$\therefore E_1 = \frac{hc}{\lambda_1} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}} = 6.626 \times 10^{-19} \text{ J}$$

$$\text{and } E_2 = \frac{hc}{\lambda_2} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{600 \times 10^{-9} \text{ m}} = 3.313 \times 10^{-19} \text{ J}$$

The ratio of E_1 and E_2 is

$$\frac{E_1}{E_2} = \frac{6.626 \times 10^{-19} \text{ J}}{3.313 \times 10^{-19} \text{ J}} = 2$$

$$\therefore E_1 = 2E_2$$

ILLUSTRATION 4.32

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz

Sol. $E = h\nu$

$$= (6.626 \times 10^{-34} \text{ J s}) (5 \times 10^{14} \text{ s}^{-1})$$

$$= (3.313 \times 10^{-19} \text{ J})$$

Energy of one mole of photons

$$= (3.313 \times 10^{-19} \text{ J}) (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$= 199.51 \text{ kJ mol}^{-1}$$

ILLUSTRATION 4.33

A 100 Watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Sol. Power of the bulb = 100 watt

$$= 100 \text{ J s}^{-1}$$

Energy of one photon:

$$E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ ms}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= 4.969 \times 10^{-19} \text{ J}$$

Number of photon emitted

$$= \frac{100 \text{ J s}^{-1}}{4.969 \times 10^{-19} \text{ J}} = 2.012 \times 10^{20} \text{ s}^{-1}$$

ILLUSTRATION 4.34

Calculate the number of protons emitted in 10 hours by a 60 W sodium lamp (λ of photon = 5893 Å)

Sol. Energy emitted by sodium lamp in 1 s.

$$= \text{Watt} \times \text{second} = 60 \times 1 \text{ J}$$

Energy of photon emitted = $\frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{5893 \times 10^{-10}}$$

$$= 3.37 \times 10^{-19} \text{ J}$$

$$\therefore \text{Number of photons emitted per second} = \frac{60}{3.37 \times 10^{-19}}$$

$$\therefore \text{Number of photons emitted in 10 hours}$$

$$= 17.8 \times 10^{19} \times 10 \times 60 \times 60$$

$$= 6.41 \times 10^{24}$$

ILLUSTRATION 4.35

An Electromagnetic radiation of wave-length 242 nm is just sufficient to ionise a sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1} .

Sol. Energy associated with a photon of 242 nm

$$= \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{242 \times 10^{-9}}$$

$$= 8.21 \times 10^{-19} \text{ J}$$

Since one atom of Na requires $= 8.21 \times 10^{-19} \text{ J}$ for ionisation,
 6.023×10^{23} atoms of Na for ionisation requires
 $8.21 \times 10^{-19} \times 6.023 \times 10^{23} = 49.45 \times 10^4 \text{ J}$
 $= 494.5 \text{ kJ mol}^{-1}$

ILLUSTRATION 4.36

A bulb emits light of wavelength 4500 Å. The bulb is rated as 150 W and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?

Sol. A 150 W bulb emits 150 J of energy per second.

The energy emitted by the bulb as light is

$$150 \times \frac{8}{100} = 12 \text{ J}$$

Let the bulb emit n photons per second.

$$E = nh\nu = \frac{nhc}{\lambda}$$

$$\therefore n = \frac{E \times \lambda}{c \times h}$$

$$= \frac{12 \text{ J} \times 4500 \times 10^{-10} \text{ m}}{3 \times 10^8 \text{ m s}^{-1} \times 6.63 \times 10^{-34} \text{ J s}}$$

$$= 2.715 \times 10^{19}$$

ILLUSTRATION 4.37

I. Electronic energy is a negative energy because

- Electron carries negative charge.
- Energy is zero near the nucleus and decreases as the distance from the nucleus increases.
- Energy is zero at an infinite distance from the nucleus and decreases as the electron comes closer to the nucleus.
- There are interelectronic repulsions.

II. Which of the following relates to photons both as an wave motion and as a stream of particles?

- a. Interference b. $E = mc^2$ c. Diffraction d. $E = h\nu$

III. Which of the following is not a characteristic of Planck's quantum theory of radiation?

- Energy is not absorbed or emitted in whole number multiples of quantum.
- Radiation is associated with energy.
- Radiation is associated with energy emitted or absorbed continuously but in the form of small packets called quanta.
- The magnitude of energy associated with quantum is proportional to frequency.

Sol.

- a. Energy is zero at an infinite distance from the nucleus and decreases as the electron comes closer to the nucleus.
- d. $E = h\nu$
- a. Energy is not absorbed or emitted in whole number multiples of quantum.

4.20 PHOTOELECTRIC EFFECT

In 1887, H. Hertz performed an experiment and observed that when a beam of light of suitable wavelength or frequency is allowed to fall on the surface of a metal (such as Cs, K, and Rb), electrons are emitted (or ejected) from the surface of the metal as shown in Fig. 4.16. This phenomenon of emission of electrons is known as photoelectric effect. The electrons emitted are known as photoelectrons.

The results of this experiment are as follows:

- Electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time gap between the striking of light beam and the ejection of electrons from the metal surface.
- The number of electrons ejected is proportional to the intensity or brightness of light.
- For each metal, there is a characteristic minimum frequency, ν_0 (also known as threshold frequency), below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with an increase in frequency of the light used.

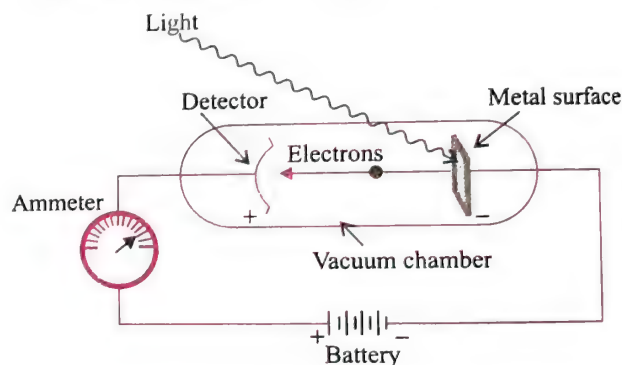


Fig. 4.16(a) Equipment for studying photoelectric effect; Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector, which measures their kinetic energies

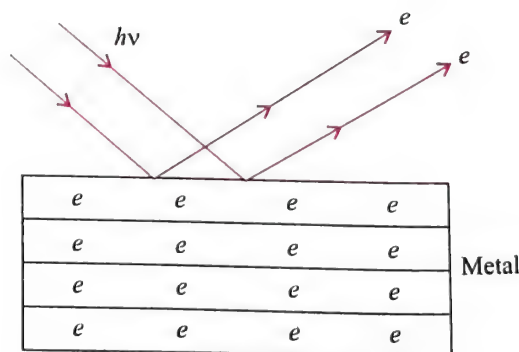


Fig. 4.16 (b) Photoelectric effect

All the above results could not be explained on the basis of laws of wave theory or classical physics, according to which the energy content of the beam of light depends upon the brightness of the light. In other words, the number of electrons ejected and the kinetic energy associated with them depend upon the brightness of light. In practice, it is found that although the number of electrons ejected depends on the intensity of the incident light, their kinetic energies do not depend.

It was Einstein (1905) who explained the photoelectric effect using Planck's quantum theory of electromagnetic radiation. According to him, electrons in metals are held by some attractive forces. To overcome these forces, a certain minimum amount of energy is required, which is characteristic of the metal.

This is called photoelectric work function, W_0 . To cause ejection of electrons, the photons of incident light should have energy equal to or greater than this work function. Since from quantum theory we know that the energy of photon is directly proportional to the frequency of radiation, the incident photons should have a certain minimum frequency called **threshold frequency or critical frequency** (ν_0).

$h\nu_0$ = photoelectric work function, W_0

When a photon of sufficient energy strikes an electron of the atom of the metal, it transfers its energy instantaneously to the electron during the collision, and the electron is ejected without any delay. If the photon has energy more than the energy required to remove the electron, then the excess of energy is taken up by the electron as kinetic energy (KE). The greater the energy possessed by photon, the greater the transfer of energy to the electron and the greater the kinetic energy of the ejected electron. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (work function W_0), the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by

$$h\nu = h\nu_0 + \text{KE}$$

$$h\nu = h\nu_0 + \frac{1}{2}m_e v^2$$

where m_e is the mass of electron and v is the velocity of the ejected electron.

$$\text{or KE} = h\nu - h\nu_0 = h(\nu - \nu_0)$$

$$\text{KE} = \frac{hc}{\lambda} - \frac{hc}{\lambda_0} = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right)$$

The kinetic energy of photoelectrons is independent of intensity because an increase in intensity does not affect the energy of photons; rather, it simply increases the number of photons falling on the surface of metal and, hence, increases the number of photoelectrons.

The photoelectric work function depends upon the nature of the metal. A metal having a higher ionisation energy has a greater value of photoelectric work function. The values of photoelectric work functions of some metals are given below:

Table 4.4 Values of work function (W_0) of a few metals

Metal	Li	Na	K	Mg	Cu	Ag
W_0/eV	2.42	2.3	2.25	3.7	4.8	4.3

ILLUSTRATION 4.38

In a photoelectric effect experiment, irradiation of a metal with light of frequency $5.2 \times 10^{14} \text{ s}^{-1}$ yields electrons with maximum kinetic energy $1.3 \times 10^{-19} \text{ J}$. Calculate the threshold frequency (ν_0) for the metal.

Sol. We know that

$$h\nu = h\nu_0 + \text{KE}$$

$$\text{or } \nu_0 = \nu - \frac{\text{KE}}{h}$$

$$\text{KE} = 1.3 \times 10^{-19} \text{ J}; \nu = 5.2 \times 10^{14} \text{ s}^{-1};$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

\therefore Threshold frequency

$$\begin{aligned} \nu_0 &= 5.2 \times 10^{14} \text{ s}^{-1} - \frac{1.3 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \\ &= 5.2 \times 10^{14} \text{ s}^{-1} - 1.96 \times 10^{14} \text{ s}^{-1} \\ &= 3.24 \times 10^{14} \text{ s}^{-1} \end{aligned}$$

ILLUSTRATION 4.39

Light of wavelength 5000 Å falls on a metal surface of work function 1.9 eV. Find

- The energy of photons.
- The kinetic energy of photoelectrons.

Sol. Wavelength of light (λ) = 5000 Å = $5 \times 10^{-7} \text{ m}$
Work function ($h\nu_0$) = 1.9 eV = $1.9 \times 1.6 \times 10^{-19} \text{ J}$
 $= 3.4 \times 10^{-19} \text{ J}$

$$\lambda \text{ in nm} = 5 \times 10^{-7} \text{ m} / 10^{-9} \text{ nm} = 500 \text{ nm}$$

- Energy of photons

$$\begin{aligned} E &= h\nu = \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (3 \times 10^8 \text{ m s}^{-1})}{5 \times 10^{-7} \text{ m}} \\ &= 3.97 \times 10^{-19} \text{ J} \\ &= \frac{3.97 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J}} = 2.48 \text{ eV} \end{aligned}$$

$$(\because 1.6 \times 10^{-19} \text{ J} = 1 \text{ eV})$$

Alternatively

Using direct relation, we get

$$\begin{aligned} E &= \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{\lambda \text{ nm}} \\ &= \frac{1240}{500} = 2.48 \text{ eV} \end{aligned}$$

b. Kinetic energy of photoelectrons

$$\begin{aligned}
 \text{KE} &= \frac{1}{2}mv^2 \\
 &= h\nu - h\nu_0 \\
 &= (3.97 \times 10^{-19} \text{ J}) - (3.4 \times 10^{-19} \text{ J}) \\
 &= 5.7 \times 10^{-20} \text{ J}
 \end{aligned}$$

ILLUSTRATION 4.40

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1.68 \times 10^5 \text{ J mol}^{-1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

Sol. Wavelength of radiation = $300 \times 10^{-9} \text{ m}$

Energy of radiation

$$\begin{aligned}
 E &= h\nu = \frac{hc}{\lambda} \\
 &= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}} \\
 &= 6.626 \times 10^{-19} \text{ J}
 \end{aligned}$$

Energy of one mole of photons

$$\begin{aligned}
 &= N_A \times E \text{ (where } N_A = \text{Avogadro number)} \\
 &= 6.022 \times 10^{23} \times 6.626 \times 10^{-19} \text{ J mol}^{-1} \\
 &= 3.99 \times 10^5 \text{ kJ mol}^{-1}
 \end{aligned}$$

The minimum energy needed to remove one mole of electrons from sodium = $(3.99 - 1.68) \times 10^5 \text{ J mol}^{-1} = 2.31 \times 10^5 \text{ J mol}^{-1}$

The minimum energy for one electron

$$\begin{aligned}
 &= \frac{2.31 \times 10^5 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons}} \\
 &= 3.84 \times 10^{-19} \text{ J mol}^{-1}
 \end{aligned}$$

This corresponds to the wavelength

$$\therefore \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ ms}^{-1}}{3.84 \times 10^{-19} \text{ J}} = 517 \text{ nm}$$

This corresponds to green light.

ILLUSTRATION 4.41

A photon of 300 nm is absorbed by a gas, which then re-emits two photons. One re-emitted photon has a wavelength of 400 nm. Calculate the energy of the other photon re-emitted out.

Sol.

$$\begin{aligned}
 E_{\text{Total}} &= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}} \\
 &= 6.626 \times 10^{-19} \text{ J} \\
 E_1 &= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} \\
 &= \frac{3}{4} \times 6.626 \times 10^{-19}
 \end{aligned}$$

$$\begin{aligned}
 E_2 &= (E_{\text{Total}} - E_1) \\
 &= 6.626 \times 10^{-19} \times \left(1 - \frac{3}{4}\right) = \frac{1}{4} \times 6.626 \times 10^{-19} \text{ J} \\
 &= 1.656 \times 10^{-19} \text{ J}
 \end{aligned}$$

ILLUSTRATION 4.42

When a certain metal was irradiated with light of frequency $4.0 \times 10^{16} \text{ s}^{-1}$, the photoelectrons emitted had three times the kinetic energy as the kinetic energy of photoelectrons emitted when the metal was irradiated with light of frequency $2.0 \times 10^{16} \text{ s}^{-1}$. Calculate the critical frequency (ν_0) of the metal.

Sol. Using Einstein's photoelectron equation,

$$\text{KE} = h\nu - h\nu_0 = h(\nu - \nu_0)$$

$$\text{KE}_1 = h(\nu_1 - \nu_0) \quad \dots(i)$$

$$\text{KE}_2 = h(\nu_2 - \nu_0) \quad \dots(ii)$$

Dividing equation (ii) by (i), we get

$$\frac{\text{KE}_2}{\text{KE}_1} = \frac{h(\nu_2 - \nu_0)}{h(\nu_1 - \nu_0)} = \frac{(\nu_2 - \nu_0)}{(\nu_1 - \nu_0)}$$

But given that

$$\frac{\text{KE}_2}{\text{KE}_1} = 3$$

$$\therefore 3 = \frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} \Rightarrow 3(\nu_1 - \nu_0) = \nu_2 - \nu_0$$

$$\Rightarrow 3\nu_1 - \nu_2 = 3\nu_0 - \nu_0 = 2\nu_0$$

$$\Rightarrow 3 \times 2.0 \times 10^{16} - 4 \times 10^{16} = 2\nu_0$$

$$\Rightarrow \nu_0 = \frac{2 \times 10^{16}}{2} = 1 \times 10^{16} \text{ s}^{-1}$$

ILLUSTRATION 4.43

I. If the threshold frequency of a metal for photoelectric effect is ν_0 , then which of the following will not happen?

- If the frequency of the incident radiation is ν_0 , the kinetic energy of the electrons ejected is zero.
- If the frequency of the incident radiation is ν , the kinetic energy of the electrons ejected will be $h\nu - h\nu_0$.
- If the frequency is kept same at ν but intensity is increased, the number of electrons ejected will increase.
- If the frequency of incident radiation is further increased, the number of photoelectrons ejected will increase.

II. The dissociation energy of H_2 is $430.53 \text{ kJ mol}^{-1}$. If H_2 is dissociated by illumination with radiation of wavelength 253.7 nm, the fraction of the radiant energy which will be converted into kinetic energy is given by

- 8.86%
- 2.33%
- 1.3%
- 90%

III. Light of wavelength λ shines on a metal surface with intensity X , and the metal emits Y electrons per second of average energy Z . What will happen to Y and Z if X is doubled?

- Y will be doubled and Z will become half.
- Y will remain same and Z will be doubled.
- Both Y and Z will be doubled.
- Y will be doubled but Z will remain same.

Sol.

- I. d. If the frequency of incident radiation is further increased, the number of photoelectrons ejected will increase.

$$\text{II. a. } \frac{hc}{\lambda} = \frac{430.53 \times 10^3}{6.023 \times 10^{23}} + \text{KE}$$

$$\begin{aligned} \text{KE} &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{253.7 \times 10^{-9}} \\ &= \frac{430.53 \times 10^3}{6.023 \times 10^{23}} = 6.9 \times 10^{-20} \end{aligned}$$

$$\therefore \text{Fraction} = \frac{6.9 \times 10^{-20}}{7.83 \times 10^{-19}} = 0.088 = 8.86$$

- III. d. When intensity is doubled, the number of electrons emitted per second is also doubled, but the average energy of photoelectrons emitted remains the same.

ILLUSTRATION 4.44

The threshold frequency ν_0 for a metal is $7.0 \times 10^{14} \text{ s}^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15} \text{ s}^{-1}$.

Sol. According to Einstein's equation.

$$\begin{aligned} \text{Kinetic energy} &= \frac{1}{2} m_e v^2 \\ &= h(\nu - \nu_0) \\ &= (6.626 \times 10^{-34} \text{ Js}) \times \\ &\quad (1.0 \times 10^{15} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1}) \\ &= (6.626 \times 10^{-34} \text{ Js}) \times \\ &\quad (1.0 \times 10^{14} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1}) \\ &= (6.626 \times 10^{-34} \text{ Js}) \times \\ &\quad (3.0 \times 10^{14} \text{ s}^{-1}) \\ &= 1.988 \times 10^{-19} \text{ J} \end{aligned}$$

ILLUSTRATION 4.45

When a certain metal was irradiated with light of frequency $1.6 \times 10^{16} \text{ Hz}$, the photoelectrons emitted had twice the kinetic energy as the photoelectrons emitted when the same metal was irradiated with light of frequency $1.0 \times 10^{16} \text{ Hz}$. Calculate the threshold frequency (ν_0) for the metal.

Sol. $h\nu = h\nu_0 + \text{KE}$

$$\text{KE}_1 = h(\nu - \nu_0)$$

$$\text{KE}_2 = h(\nu_2 - \nu_0) = \frac{\text{KE}_1}{2}$$

$$\therefore \frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} = \frac{1}{2} \Rightarrow \frac{1.0 \times 10^{16} - \nu_0}{1.6 \times 10^{16} - \nu_0} = \frac{1}{2}$$

$$\Rightarrow \nu_0 = 4 \times 10^{15} \text{ Hz}$$

ILLUSTRATION 4.46

Calculate the energy in kilojoules per mole of electronic charge accelerated by a potential of 1 V.

$$\begin{aligned} \text{Sol. Energy in joules} &= \text{change in coulombs} \\ &\quad \times \text{potential difference in volt} \\ &= 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \times 1 \\ &= 9.632 \times 10^4 \text{ J or } 96.32 \text{ kJ} \end{aligned}$$

ILLUSTRATION 4.47

An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 \AA .

Sol. For an electron

$$\frac{1}{2} m v^2 = eV$$

where V is the accelerating potential.

$$\lambda = \frac{h}{mv}$$

$$\therefore \frac{1}{2} m \left(\frac{h}{m\lambda} \right)^2 = eV$$

$$\therefore V = \frac{1}{2} \times \frac{h^2}{m\lambda^2 e}; \text{ substituting all values, we get}$$

$$\begin{aligned} &= \frac{1 \times (6.625 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}} \\ &= 63.3 \text{ V} \end{aligned}$$

ILLUSTRATION 4.48

The eyes of a reptile pass a visual signal to the brain when the visual receptors are struck by photons of wavelength 859 nm . If an energy of $3.15 \times 10^{-14} \text{ J}$ is required to trip the signal, what is the minimum number of photons that must strike the receptor ($h = 6.6 \times 10^{-34} \text{ Js}$)?

$$\text{Sol. } E = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{850 \times 10^{-9}} = 2.3 \times 10^{-19} \text{ J}$$

$$\text{Energy required to trip signal} = 3.15 \times 10^{-14} \text{ J}$$

$$n \times E = E_{\text{total}}; \text{ photons that strike the receptor are}$$

$$n = \frac{3.15 \times 10^{-14}}{2.3 \times 10^{-19}} = 1.37 \times 10^5 \text{ photons}$$

ILLUSTRATION 4.49

A dye absorbs light of $\lambda = 4530 \text{ \AA}$ and then fluorescence light of 5080 \AA . Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorescence, calculate the ratio of quanta emitted out to the number of quanta absorbed.

$$\begin{aligned} \text{Sol. We know, energy of light absorbed in one photon} \\ &= \frac{hc}{\lambda_{\text{Absorbed}}} \end{aligned}$$

Let n_1 photons be absorbed. Therefore

$$\text{Total energy absorbed} = \frac{n_1 hc}{\lambda_{\text{Absorbed}}}$$

Now, energy of light re-emitted then,

$$\text{Total energy re-emitted out} = n_2 \times \frac{hc}{\lambda_{\text{Emitted}}}$$

$$\text{As given } E_{\text{Absorbed}} \times \frac{47}{100} = E_{\text{Re-emitted out}}$$

$$\frac{\lambda c}{\lambda_{\text{Absorbed}}} \times n_1 \times \frac{47}{100} = \frac{\lambda_{\text{Emitted}}}{\lambda_{\text{Absorbed}}}$$

$$\frac{n_2}{n_1} = \frac{47}{100} \times \frac{5080}{4530} = 0.527$$

4.21 DUAL NATURE OF ELECTROMAGNETIC RADIATIONS

As discussed above, black body radiation and photoelectric effect could be explained satisfactorily on considering that electromagnetic radiations consist of particles. On the other hand, radiations exhibit phenomena of reflection, refraction, dispersion, interference and diffraction, which indicate that they possess wave nature. So it may be concluded that electromagnetic radiations possess dual nature, i.e., particle nature as well as wave nature. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle-like properties in contrast to wave-like properties (interference and diffraction), which it exhibits while propagating.

Einstein (1905) calculated the mass of photon associated with a radiation of frequency ν as given below:

The energy E of the photon is given by

$$E = h\nu \quad \dots(i)$$

Also according to Einstein's equation

$$E = mc^2 \quad \dots(ii)$$

where m is the mass of photon.

From equations (i) and (ii), we get

$$h\nu = mc^2$$

$$m = \frac{h\nu}{c^2} \quad \dots(iii)$$

$$\text{or } m = \frac{h}{c^2} \cdot \frac{c}{\lambda}$$

$$m = \frac{h}{c\lambda} \quad \dots(iv)$$

Equations (iii) and (iv) show the relationship between mass and wavelength of photon.

ILLUSTRATION 4.50

Calculate the mass of a photon of sodium light having wavelength 600 nm and velocity $3 \times 10^8 \text{ m s}^{-1}$.

Sol. Wavelength of photon,

$$\lambda = 600 \times 10^{-9} \text{ m} = 6.0 \times 10^{-7} \text{ m}$$

$$\text{Velocity of photon } (v) = 3 \times 10^8 \text{ m s}^{-1}$$

Using relationship

$$m = \frac{h}{c\lambda}$$

We get

$$\begin{aligned} \text{Mass of photon} &= \frac{6.626 \times 10^{-34} \text{ J s}}{3 \times 10^8 \text{ m s}^{-1} \times 6.0 \times 10^{-7} \text{ m}} \\ &= 3.68 \times 10^{-36} \text{ kg} \end{aligned}$$

ILLUSTRATION 4.51

The kinetic energy of an electron is $4.55 \times 10^{-25} \text{ J}$. The mass of electron is $9.1 \times 10^{-31} \text{ kg}$. Calculate velocity of the electron.

Sol. Calculation of the velocity of electron:

$$\begin{aligned} \text{Kinetic energy} &= \frac{1}{2}mv^2 = 4.55 \times 10^{-25} \text{ J} \\ &= 4.55 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2} \end{aligned}$$

$$\text{or } v^2 = \frac{2 \times \text{KE}}{m} = \frac{2 \times (4.55 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2})}{(9.1 \times 10^{-31} \text{ kg})}$$

$$= 10^6 \text{ m}^2 \text{ s}^{-2}$$

$$\text{or velocity } (v) = (10^6 \text{ m}^2 \text{ s}^{-2})^{\frac{1}{2}} = 10^3 \text{ m s}^{-1}$$

ILLUSTRATION 4.52

What will be the kinetic energy and total energy change of an electron in H atom if the atom emits a photon of wavelength 4860 Å?

Sol. The energy released is

$$\begin{aligned} E &= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (3 \times 10^8 \text{ m s}^{-1})}{(4860 \times 10^{-10} \text{ m})} \\ &= 4.09 \times 10^{-19} \text{ J} \end{aligned}$$

$$\therefore \text{Total energy change} = 4.09 \times 10^{-19} \text{ J}$$

Loss in energy due to release of photon = gain in kinetic energy = $4.09 \times 10^{-19} \text{ J}$

ILLUSTRATION 4.53

Find the ratio of frequencies of violet light ($\lambda_1 = 4.10 \times 10^{-5} \text{ cm}$) to that of red light ($\lambda_2 = 6.56 \times 10^{-5} \text{ cm}$). Also determine the ratio of energies carried by them.

Sol. Using $c = \nu\lambda$

where c is speed of light, ν is frequency, λ is wavelength

$$\frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1} \quad [1 : \text{violet and } 2 : \text{red}]$$

$$\Rightarrow \frac{\nu_1}{\nu_2} = \frac{6.56 \times 10^{-5}}{4.10 \times 10^{-5}} = 1.6 : 1$$

Now the energy associated with electromagnetic radiation is given by $E = h\nu$. Therefore,

$$\frac{E_1}{E_2} = \frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1} = 1.6 : 1$$

Hence, the ratio of energies is same as that of frequencies.

4.22 EVIDENCE FOR QUANTISED ELECTRONIC ENERGY LEVELS: ATOMIC SPECTRA

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium

to another. It is observed that when a ray of white light is passed through a prism, it undergoes deviation. The angle of deviation is directly proportional to the frequency of radiation. Since ordinary white light consists of waves with all wavelength/frequencies in the visible range, it undergoes unequal deviation and gets arranged in order of decreasing frequencies, i.e., a beam of ordinary light splits up into seven colours (VIBGYOR) after passing through a prism. This phenomenon of splitting of a beam of light into radiations of different frequencies after passing through a prism is called dispersion, and the pattern of radiations obtained after dispersion is called spectrum.

In case of ordinary white light, the red colour with the longest wavelength is deviated the least while the violet colour with the shortest wavelength is deviated the most. The spectrum of white light that we can see ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. This spectrum is called *continuous spectrum* because violet merges into blue, blue into green, and so on. A similar spectrum is produced when a rainbow forms in the sky.

In a continuous spectrum, radiations corresponding to all the wavelengths (within a certain range) are present. The visible light is just a fraction of the electromagnetic radiation. When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and get excited to a higher energy state. For returning to their more stable energy states, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

4.22.1 EMISSION AND ABSORPTION SPECTRA

When a sample is subjected to heating or irradiation, it absorbs radiation or energy and gets excited. As the sample gives up the absorbed energy, the wavelength (or frequency) of the radiation emitted is recorded.

The arrangement of these radiations in the order of increasing wavelengths or decreasing frequencies is called **emission spectrum**. Since the radiations in the spectrum are emitted due to energy changes taking place in the atoms, this spectrum is also known as atomic spectrum.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiations is passed through a sample, which absorbs radiation of certain wavelengths. The missing wavelength that corresponds to the radiation absorbed by matter leaves dark spaces in the bright continuous spectrum (Figs. 4.17 and 4.18).

The study of emission or absorption spectra is referred to as **spectroscopy**. The instrument used for obtaining a spectrum is called **spectroscope or spectrograph**. The spectrum of the visible light, as discussed above, is a continuous spectrum. On the other hand, the emission spectra of atoms in the gas phase do not show a continuous spread of wavelength from red to violet; rather, they emit light only at specific wavelengths with dark spaces between them. Such spectra are also known as line spectra or atomic spectra. The various lines in the line spectrum correspond to the radiations of different wavelengths emitted by the excited element. The lines

in the line spectrum of an element are characteristic of the atoms of an element. These characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms. Therefore, the atomic spectrum of an element is sometimes called **fingerprint** of its atoms. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample easily establishes the identity of the latter. German chemist, Robert Bunsen (1811–1899) was one of the first investigators to use line spectra to identify elements.

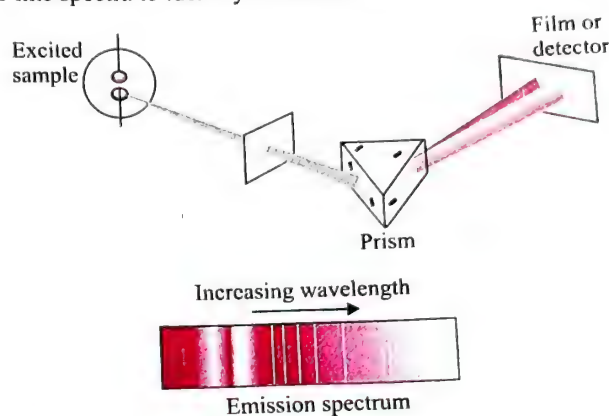


Fig. 4.17 Atomic emission: The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths, is called a line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum.

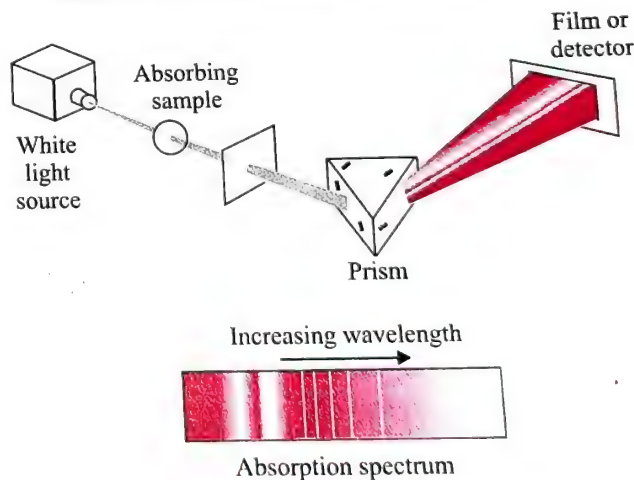


Fig. 4.18 Atomic absorption: When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light lacks in intensity at the same wavelength as are emitted in Fig. 4.17. The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

Elements such as rubidium (Rb), caesium (Cs), thallium (Tl), indium (In), gallium (Ga), and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

4.23 HYDROGEN SPECTRUM

The atomic spectrum of hydrogen has been proved to be very helpful in the development of atomic structure. When an electric discharge is passed through hydrogen gas, its molecules dissociate into hydrogen atoms. An energetically excited hydrogen atom then emits electromagnetic radiation of discrete frequencies. The spectrum obtained consists of a large number of sharp lines. Each line corresponds to a particular frequency of light emitted by hydrogen atoms. The *lines* of hydrogen spectrum are named after their discoverers. Lines in the emission spectrum of hydrogen are present in ultraviolet, visible, and infrared regions.

Balmer showed in 1885 that if spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the expression

$$\bar{\nu} = 109677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{cm}^{-1}$$

where n is an integer equal to or greater than 3 (i.e., $n = 3, 4, 5, \dots$). The series of lines that could be described by this expression are known as *Balmer series*. Later, a Swedish spectroscopist Johannes Rydberg gave a more general expression applicable to all the series in the hydrogen spectrum:

$$\bar{\nu} = 109677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$$

where n_1 and n_2 are integers such that $n_2 > n_1$. The value of 109677 cm^{-1} is called the Rydberg constant (R) for hydrogen. For a particular series, n_1 is constant.

Table 4.5 Series of transitions in hydrogen spectrum

Series of lines	n_1	n_2	Spectral region	Wavelength
Lyman series	$n_1 = 1$	$n_2 = 2, 3, 4, \dots \infty$	UV light	$< 4000 \text{ \AA}$
Balmer series	$n_1 = 2$	$n_2 = 3, 4, 5, \dots \infty$	Visible	$4000\text{--}7000 \text{ \AA}$
Paschen series	$n_1 = 3$	$n_2 = 4, 5, 6, \dots \infty$	Near infrared	$> 7000 \text{ \AA}$
Bracket series	$n_1 = 4$	$n_2 = 5, 6, 7, \dots \infty$	Infrared	$> 7000 \text{ \AA}$
Pfund series	$n_1 = 5$	$n_2 = 6, 7, 8, \dots \infty$	Far infrared	$> 7000 \text{ \AA}$
Humphrey series	$n_1 = 6$	$n_2 = 7, 8, 9, \dots \infty$	Far infrared	$> 7000 \text{ \AA}$

Table 4.5 shows these series of transitions in the hydrogen spectrum. Figure 4.19 shows the Lyman, Balmer, and Paschen series of transitions for a hydrogen atom.

A hydrogen atom has the simplest atomic spectrum. A heavier atom has more and more complex atomic spectrum or line spectrum. However, there are certain features common to all line spectra, viz.

- Line spectrum of an element is unique and
- There is a regularity in the line spectrum of each element

Table 4.6 The spectral lines for atomic hydrogen

Series	n_1	n_2	Spectral region
Lyman	1	2, 3, ...	Ultraviolet
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	Infrared
Brackett	4	5, 6, ...	Infrared
Pfund	5	6, 7, ...	Infrared
Humphrey	6	7, 8, ...	Far infrared

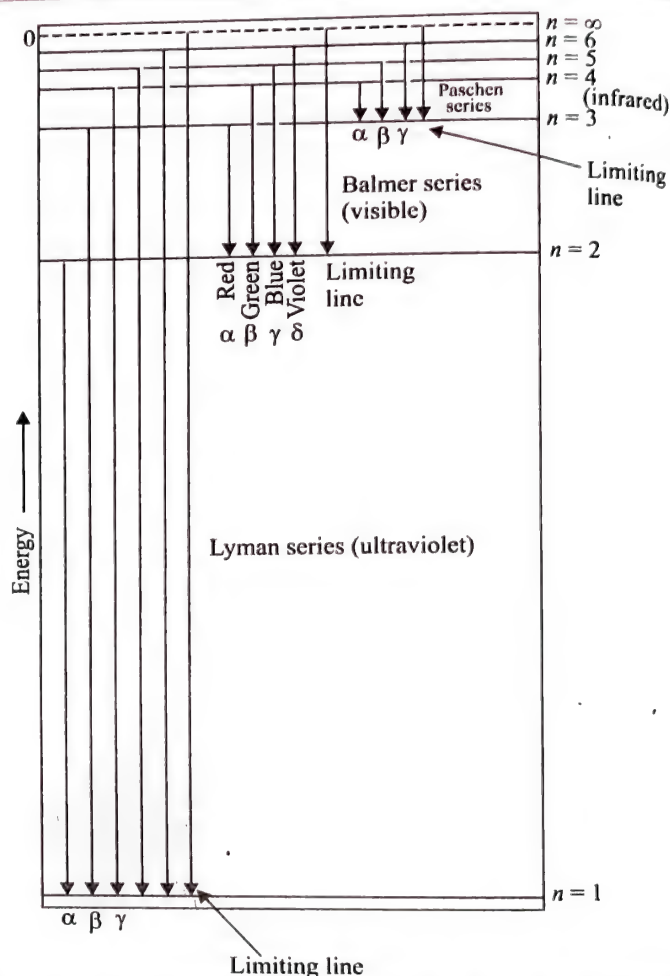


Fig. 4.19 Transitions of electron in a hydrogen atom (The diagram shows the Lyman, Balmer, and Paschen series of transitions.)

For the given value of n (principal quantum number), the total number of spectral lines can be calculated by the expression $n(n-1)/2$.

Note:

- R is known as the Rydberg constant. Its value to be used is $= 109677 \text{ cm}^{-1} = 10967700 \text{ m}^{-1} = 1 \times 10^7 \text{ m}^{-1}$.
- The value of $1/R \approx 911.5 \text{ \AA}$ is sometimes useful.
- This relation exactly matches with the empirical relation given by Balmer and Rydberg to account for the spectral lines in H atom spectra. In fact the value of Rydberg constant in the empirical relation

is approximately the same as calculated from Bohr's theory. This was the main success of Bohr's theory, i.e., to account for the experimental observations by postulating a theory.

- d. The maximum number of lines that can be emitted when an electron in an excited state $n = n_2$ de-excites to a state $n = n_1$ ($n_2 > n_1$) is given by

$$\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$$

4.24 BOHR'S MODEL FOR HYDROGEN ATOM

In 1913, **Niels Bohr**, a Danish physicist, proposed a model of an atom based on classical and early quantum physics in order to overcome the shortcomings of the Rutherford model.

Bohr retained Rutherford's concept of a central positive charged nucleus surrounded by a planetary system of electrons. He also made use of Planck's quantum theory. The main postulates of Bohr's theory are as follows:

- a. The electron in the hydrogen atom revolves around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states, energy shells, or allowed energy states. These stationary states for electrons are numbered as $n = 1, 2, 3, \dots$ or designated as K, L, M, N, ..., etc. shells (Fig. 4.20). These integral numbers are known as principal quantum numbers. These orbits are arranged concentrically around the nucleus.

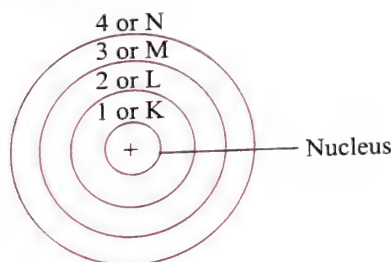


Fig 4.20 Bohr's orbit

- b. Electrons revolve only in those orbits where the angular momentum of the electron is quantized. Thus an electron can move only in those orbits for which its angular momentum is an integral multiple of $h/2\pi$ that is why only certain fixed orbitals are allowed.

$$m_e v r = n \frac{h}{2\pi}, \quad \text{or} \quad n \hbar \quad \left(\text{where } \hbar = \frac{h}{2\pi} \right)$$

where $n = 1, 2, 3, \dots, n$; h is Planck's constant; m is mass of electron; v is the velocity of electron; and r is the radius of the orbit.

- c. The energy of an electron in the orbit does not change with time. This means that the energy of an electron in a particular orbit remains constant; it does not lose or gain energy.
- d. The electron will move from a lower stationary state to a higher stationary state when the required amount of energy is absorbed by the electron. When the electron jumps back to the lower energy level, it emits the same amount of energy.

The energy change does not take place in a continuous manner.

- e. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE is given by

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h},$$

where E_1 and E_2 are the energies of the lower and higher allowed energy states, respectively. This expression is called Bohr's frequency rule.

- f. According to Bohr's theory for hydrogen atom:

- i. The stationary states for electron are numbered. $n = 1, 2, 3, \dots$. These integral numbers are known as Principal quantum numbers.

- ii. The radii of the stationary states are expressed as:

$$r_n = n^2 a_0$$

where $a_0 = 52.9$ pm. Thus the radius of first stationary states called the **Bohr orbit** is 52.9 pm. Electron in the hydrogen atom is found in this orbit (i.e., $n = 1$)

As n increases the value of r will increase i.e. electron will be present away from the nucleus.

- iii. Energy of electron of its stationary state is:

$$E_n = -R_H \left(\frac{1}{n^2} \right), \quad n = 1, 2, 3, \dots$$

where R_H is called **Rydberg constant** and its value is 2.18×10^{-18} J and this is the energy of hydrogen atom.

Similarly, energy of stationary state for $n = 2$ is

$$E_2 = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} \right) = -0.545 \times 10^{-18} \text{ J}$$

4.24.1 EXPLANATION OF LINE SPECTRUM OF HYDROGEN

Line spectrum of hydrogen atom can be explained quantitatively by using Bohr's theory. Energy (radiation) is absorbed if the electron moves from smaller value of n to higher value of n . (Principal quantum number), whereas energy (radiation) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between two orbits is given as:

$$\Delta E = E_f - E_i \quad (i)$$

Energy of electron of its stationary state is:

$$E_n = -R_H \left(\frac{1}{n^2} \right), \quad n = 1, 2, 3, \dots \quad (ii)$$

Combining equations (i) and (ii), we get

$$\Delta E = \left(\frac{-R_H}{n_f^2} \right) - \left(\frac{-R_H}{n_i^2} \right) \quad (iii)$$

where n_i and n_f stand for initial orbit and final orbits.

$$\begin{aligned} \Delta E &= R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \end{aligned}$$

The frequency (ν) associated with the absorption and emission of the photon is expressed as:

$$\begin{aligned}\nu &= \frac{\Delta E}{h} = \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} \\ &= 3.29 \times 10^{15} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)\end{aligned}$$

and in terms of wave-number ($\bar{\nu}$)

$$\begin{aligned}\bar{\nu} &= \frac{\nu}{c} = \frac{R_H}{h_c} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{3.29 \times 10^{15} \text{ s}^{-1}}{3 \times 10^8 \text{ ms}^{-1}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ m}^{-1}\end{aligned}$$

In case of absorption spectrum, ($n_f > n_i$) and the term in parenthesis is positive and energy is absorbed. In case of emission spectrum, $n_i > n_f$, ΔE is negative and energy is released.

Note that each spectral line, whether is absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of H-atom, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wave-length or frequency absorbed or emitted.

4.24.2 SUCCESSES OF BOHR'S MODEL

a. Bohr's model could explain the stability of an atom. According to Bohr's model, an electron revolving in a particular orbit cannot lose energy. The electron can lose energy only if it jumps to some lower energy level. If no lower energy level is vacant, then the electron will keep on revolving in the same orbit without losing energy and, hence, it explains the stability of atom.

b. Bohr's theory successfully explains the hydrogen spectrum. It also explains the spectrum of some other one-electron systems (H-like system) such as He^+ , Li^{2+} , Be^{3+} , etc.

With the help of Bohr's theory, we find out

- Radius of the orbit (r_n) in which the electron is revolving around the nucleus
- Energy of the electron (E_n) in an orbit
- Velocity of the electron (V_n) in an orbit

4.24.3 WHAT DOES THE NEGATIVE ELECTRON ENERGY (E_n) MEAN?

a. The energy of an electron in a hydrogen atom has a negative sign for all possible orbits. What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free

electron at rest. An electron in an atom is because of the attractive force due to protons in the nucleus. A free electron at rest is an electron infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation, so that $E_\infty = 0$. As electron gets closer to the nucleus, E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by $n = 1$, which corresponds to the most stable orbit.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principle Quantum number $= n = \infty$ and is called as ionised hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n , the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in the equation $\left[E_n = -R_H \left(\frac{1}{n^2} \right) \right]$, $n = 1, 2, 3 \dots$ and depicts its stability relative to the reference state of zero energy and $n = \infty$.

b. Bohr's theory can also be applied to the ions containing only one electron, similar to that present in the hydrogen atoms, eg., He^+ , Li^{2+} , Be^{3+} and so on.

The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression:

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J}$$

and radii by the expression

$$r_n = \frac{52.9 \times n^2}{Z} \text{ pm}$$

where Z is the atomic number and has values 2 and 3 for He^+ and Li^{2+} ions respectively. This shows the value of energy becomes more negative and that radius becomes smaller with increase of Z . This means that electron will be tightly held to the nucleus.

c. Similarly it is also possible to calculate the velocities of the electrons moving in these orbits. It is given by the expression:

$$V_n = \frac{Ze^2}{2hn} = 2.18 \times 10^6 \times \frac{Z}{n} \text{ ms}^{-1}$$

Qualitatively the magnitude of velocity of electron increases with the increase of positive charge on the nucleus and decreases with the increase of principal quantum number.

4.24.4 EXPERIMENTAL FACTS IN FAVOUR OF BOHR'S THEORY

The points in favour of the validity of Bohr's theory are summarised as follows:

a. The frequencies of the spectral lines of the hydrogen spectrum, as determined experimentally, are in close agreement with the frequencies of the same lines calculated with the help of Bohr's theory.

- b. The value of Rydberg constant for hydrogen, R_H , as calculated from Bohr's theory ($R_H = 109677 \text{ cm}^{-1}$) is in complete agreement with the experimental value (109677 cm^{-1}) obtained from spectroscopic studies.
- c. The radii and energies of the permissible orbits in hydrogen atom as calculated from Bohr's theory are in full agreement with experimental values.

4.24.5 LIMITATIONS OF BOHR'S MODEL

Bohr's model of the hydrogen was an improvement over Rutherford's nuclear model. It could explain the stability of an atom and the line spectra of hydrogen atom and hydrogen-like ions (for example, H_2^+ , Li^{2+} , Be^{3+} , and so on). A few years later, several discrepancies were observed in Bohr's theory. Some of these are listed below:

- a. Bohr's model could not explain the spectra of atoms containing more than one electron.

- b. It was observed that in the presence of a magnetic field, each spectral line gets split into closely spaced lines. This phenomenon, known as **Zeeman effect**, could not be explained by Bohr's model.
- c. Similarly, **Stark effect**, i.e., splitting of spectral lines in presence of electric field, could not be explained by Bohr's model.
- d. In 1923, French physicist de Broglie suggested that electron, like light, has dual character. It has particle as well as wave nature. Bohr had treated electron only as a particle.
- e. The main objection to Bohr's theory was raised by **Heisenberg's uncertainty principle**. According to this principle, it is impossible to determine simultaneously the exact position and momentum of a small particle like an electron. The postulate of Bohr that electron moves in well-defined orbits around the nucleus, is therefore, not valid.
- f. Bohr's model could not explain the geometry and shapes of molecules.

Table 4.7 Relationship and Important formulae relating to Bohr's theory

S.No.	Radius	Velocity	Energy	Wavelength
1.	$r = \frac{n^2 h^2}{4\pi^2 m Z e^2}$	$V = \frac{2\pi Z e^2}{nh}$	$E = -\frac{Z e^2}{2r}$	$R = \frac{2\pi^2 m e^4}{ch^3}$
2.	$r = \frac{n^2}{Z} \times 0.529 \text{ \AA}$	$V = \left(\frac{Z e^2}{rm}\right)^{1/2}$	$E = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$	$\frac{1}{\lambda} = R \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$
3.	$r = \frac{n^2}{Z} \times 0.0529 \text{ nm}$	$V = \frac{nh}{2\pi mr}$	$E = -Rhc \times \frac{Z^2}{n^2}$	$E = h\nu$
4.	$r \propto n^2$ (Z constant)	$V \propto \frac{1}{n}$ (Z constant)	$E = -\frac{Z^2}{n^2} \times 313.6 \text{ kcal}$	$\lambda = \frac{h}{mc}$
5.	$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$ (Z constant)	$\frac{V_1}{V_2} = \frac{n_2}{n_1}$ (Z constant)	$E \propto -Z^2$ (n constant)	$c = \frac{v}{t}$
6.	$r \propto \frac{1}{Z}$ (n constant)	Time period $T = \frac{2\pi r}{V}$	$\frac{E_1}{E_2} = \frac{Z_1^2}{Z_2^2}$ (n constant)	$E = mc^2$

ILLUSTRATION 4.54

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

$$\Delta E = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{5^2} \right)$$

$$= -4.58 \times 10^{-19} \text{ J}$$

The frequency of photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h} = \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}$$

$$= 6.91 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{6.91 \times 10^{14} \text{ Hz}} = 434 \text{ nm}$$

It is an emission energy

Alternatively

If $n_1 = 2$, $n_2 = 5$

$$\Delta E = 2.18 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} - \frac{1}{2^2} \right)$$

$$= -4.58 \times 10^{-19} \text{ J}$$

ILLUSTRATION 4.55

Calculate the energy associated with the first orbit of He^{\oplus} . What is the radius of orbit?

Sol.
$$E_n = -\frac{(2.18 \times 10^{-18} \text{ J})Z^2}{n^2} \text{ atom}^{-1}$$

For He^{\oplus} , $n = 1$, $Z = 2$

$$\begin{aligned} E_1 &= \frac{-(2.18 \times 10^{-18} \text{ J})(2^2)}{1^2} \\ &= -8.72 \times 10^{-18} \text{ J} \end{aligned}$$

The radius of the orbit is given:

$$r_n = \frac{(0.0529 \text{ nm})n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$\begin{aligned} r_n &= \frac{(0.0529 \text{ nm}) \times 1^2}{2} \\ &= 0.02645 \text{ nm} \end{aligned}$$

ILLUSTRATION 4.56

What is the wavelength of the light emitted when an electron in a hydrogen atom undergoes transition from the energy level $n = 4$ to energy level $n = 2$? What is the colour corresponding to their wavelengths? (Given $R_H = 109677 \text{ cm}^{-1}$)

Sol. According to Balmer equation,

$$\text{Wavenumber } (\bar{\nu}) = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}$$

$$n_1 = 2, n_2 = 4, R_H = 109677 \text{ cm}^{-1}$$

Substituting all the values, we get

$$\bar{\nu} = 109677 \left[\frac{1}{(2)^2} - \frac{1}{(4)^2} \right] \text{ cm}^{-1} = \frac{109677 \times 3}{16} \text{ cm}^{-1}$$

$$\text{or } \lambda = \frac{1}{\bar{\nu}} = \frac{16}{109677 \times 3} \text{ cm} = 486 \text{ nm}$$

This wavelength corresponds to blue colour.

ILLUSTRATION 4.57

Calculate the wavelength of the first line in the Balmer series of hydrogen spectrum.

Sol. For the first line in Balmer series, $n_1 = 2$ and $n_2 = 3$. So

$$\begin{aligned} \bar{\nu} &= R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \\ &= 109677 \left[\frac{1}{(2)^2} - \frac{1}{(3)^2} \right] \text{ cm}^{-1} \\ &= 109677 \times \frac{5}{36} \text{ cm}^{-1} \\ &= 15232.9 \text{ cm}^{-1} \end{aligned}$$

$$\text{or } \lambda = \frac{1}{\bar{\nu}} = \frac{1}{15,232.9} \text{ cm} = 6.565 \times 10^{-5} \text{ cm} = 656.5 \text{ nm}$$

ILLUSTRATION 4.58

Calculate the shortest wavelength in H_2^{\oplus} spectrum of Lyman series when $R_H = 109,677 \text{ cm}^{-1}$.

Sol. For Lyman series, $n_1 = 1$.

For the shortest Lyman series, the energy difference in two levels showing transition should be maximum. (i.e., $n_2 = \infty$).

Using the expression

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

We get

$$\frac{1}{\lambda} = 109677 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) \text{ cm}^{-1} = 109677 \text{ cm}^{-1}$$

$$\text{or } \lambda = 911.7 \times 10^{-8} \text{ cm} = 911.7 \times 10^{-10} \text{ m} = 911.7 \text{ Å}$$

ILLUSTRATION 4.59

Find the wavelength of radiation required to excite an electron in the ground level of Li^{2+} ($Z = 3$) to the third energy level.

Sol. For Li^{2+} , transition occurs from $n_1 = 1$ to $n_2 = 3$.

$$\therefore \bar{\nu} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad [\text{for } \text{Li}^{2+}, Z = 3]$$

$$\bar{\nu} = 109677 \times 3^2 \left[\frac{1}{1^2} - \frac{1}{3^2} \right]$$

$$\bar{\nu} = 8.77 \times 10^7 \text{ m}^{-1}$$

$$\text{or } \lambda = \frac{1}{\bar{\nu}} = 113.9 \text{ Å}$$

ILLUSTRATION 4.60

What is the maximum number of emission lines when the excited electron of a H atom in $n = 6$ drops to the ground state?

Sol. The number of lines produced when an electron from the n th shell drops to the ground state is

$$\frac{n(n-1)}{2}$$

$$\text{So the required number of emission lines is } \frac{6(6-1)}{2} = 15$$

ILLUSTRATION 4.61

- I. The ionisation energy of H atom is 13.6 eV. The ionisation energy of Li^{2+} ion will be
a. 54.4 eV b. 122.4 eV c. 13.6 eV d. 27.2 eV
- II. The ionisation energy of He^{\oplus} is $19.6 \times 10^{-18} \text{ J atom}^{-1}$. The energy of the first stationary state of Li^{2+} will be
a. $84.2 \times 10^{-18} \text{ J atom}^{-1}$

b. $44.10 \times 10^{-18} \text{ J atom}^{-1}$

c. $63.2 \times 10^{-18} \text{ J atom}^{-1}$

d. $21.2 \times 10^{-18} \text{ J atom}^{-1}$

III. The shortest wavelength in H spectrum of Lyman series when $R_H = 109678 \text{ cm}^{-1}$ is

a. 1002.7 \AA

b. 1215.67 \AA

c. 1127.30 \AA

d. 911.7 \AA

IV. A spectral line in the spectrum of H atom has a wavenumber of 15222.22 cm^{-1} . The transition responsible for this radiation is (Rydberg constant $R = 109677 \text{ cm}^{-1}$)

a. $2 \rightarrow 1$

b. $4 \rightarrow 2$

c. $3 \rightarrow 2$

d. $2 \rightarrow 3$

Sol.

I. b. $E_1 \text{ for } \text{Li}^{2+} = E_1 \text{ for H} \times Z^2 \quad [\text{for Li, } Z = 3]$
 $= 13.6 \times 9 = 122.4 \text{ eV}$

II. b. $E_1 \text{ for } \text{Li}^{2+} = E_1 \text{ for H} \times Z^2 = E_1 \text{ for H} \times 9$
 $E_1 \text{ for } \text{He}^{\oplus} = E_1 \text{ for H} \times Z_{\text{He}}^2 = E_1 \text{ for H} \times 4$
 or $E_1 \text{ for } \text{Li}^{2+} = \frac{9}{4} E_1 \text{ for He}^{\oplus} = 19.6 \times 10^{-18} \times \frac{9}{4}$
 $= 44.10 \times 10^{-18} \text{ J atom}^{-1}$

III. d. For Lyman series, $n_1 = 1$.

For shortest 'wavelength' of Lyman series, the energy difference in two levels showing transition should be maximum (i.e., $n_2 = \infty$)

$$\frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = \lambda = \frac{1}{109678}$$

$$= 109678 \Rightarrow \lambda = \frac{1}{109678} \times 911.7 \times 10^{-8} = 911.7 \text{ \AA}$$

IV. c. $\lambda = \frac{1}{\bar{\nu}} = \frac{1}{15222.22} = 6.569 \times 10^{-5} \text{ cm} = 6569 \text{ \AA}$

(Visible light wavelength)

Clearly, it lies in the visible region i.e., in Balmer series. Hence, $n_1 = 2$. Using the relation for wavenumber for H atom,

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$15222.22 = 109677 \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

$$n_2 = 3$$

The required transition is $3 \rightarrow 2$.

Hence, (c) is correct.

Note: (d) is wrong because $2 \rightarrow 3$ will absorb radiation.

ILLUSTRATION 4.62

Calculate the wavelength emitted during the transition of an electron in between two levels of Li^{2+} ion whose sum is 4 and difference is 2.

Sol. Let the transition occur between levels n_1 and n_2 and $n_2 > n_1$.

Given that $n_1 + n_2 = 4$ and $n_2 - n_1 = 2$

$\therefore n_1 = 1$ and $n_2 = 3$

$$\therefore \frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{(1)^2} - \frac{1}{(3)^2} \right]$$

$$= 109,678 \times (3)^2 \left[\frac{8}{9} \right]$$

$$\therefore \lambda = 1.14 \times 10^{-6} \text{ cm}$$

ILLUSTRATION 4.63

Calculate the ratio of the wavelengths of the first and the ultimate line of the Balmer series of Li^{2+} ?

Sol.

c. Wavenumber of the first line of the Balmer series,

$$n_1 = 2 \text{ and } n_2 = 3$$

$$\bar{\nu}_1 = RZ^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{5 \times 9R}{36} = \frac{5R}{4}$$

$$\therefore \text{Wavelength of the first line of the Balmer series} = \frac{4}{5R}$$

Wavenumber of ultimate line (limiting line) of the Balmer series,

$$\bar{\nu}_2 = RZ^2 \left[\frac{1}{2^2} - \frac{1}{\infty} \right] = \frac{9R}{4}$$

$$\therefore \text{Wavelength of the ultimate line of the Balmer series} = \frac{4}{9R}$$

$$\therefore \text{Ratio} = \frac{9}{5}$$

ILLUSTRATION 4.64

What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ in the He^{\oplus} spectrum?

a. $n = 4$ to $n = 2$

b. $n = 3$ to $n = 2$

c. $n = 3$ to $n = 1$

d. $n = 2$ to $n = 1$

Sol. d. $\bar{\nu} = \frac{1}{\lambda} = \left(\frac{1}{2^2} - \frac{1}{4^2} \right) RZ^2 = \frac{3}{4} R$

In H spectrum for the same $\bar{\nu}$ or λ as $Z = 1$, $n = 1$, $n_2 = 2$

ILLUSTRATION 4.65

The wavelength of series limit for Lyman series for He^{\oplus} ion would be

- a. 911.7 Å
b. 227.9 Å
c. 1215.1 Å
d. 303.8 Å

Sol.

b. $Z = 2$ (for He^{\oplus})

Series limit for Lyman series

$$n_1 = 1, n_2 = \infty$$

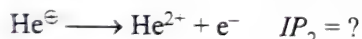
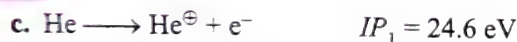
$$\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R(2)^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = 4R$$

$$\lambda = \frac{1}{4R} = \frac{1}{4 \times 109677 \text{ cm}^{-1}} = 227.9 \times 10^{-10} \text{ m} = 227.9 \text{ Å}$$

ILLUSTRATION 4.66

The energy required to ionise a helium atom is equal to 24.6 eV. The energy required to remove both the electrons from the helium atom would be

- a. 59 eV b. 81 eV c. 79 eV d. 40 eV

Sol.

$$IP_2 = 13.6 \text{ eV} \times Z^2 = 13.6 \times 2^2 = 54.4 \text{ eV}$$

$$IP_1 + IP_2 = 24.6 + 54.4 = 79 \text{ eV}$$

ILLUSTRATION 4.67

Let ν_1 be the frequency of the series limit of the Lyman series, ν_2 be the frequency of the first line of the Lyman series, and ν_3 be the frequency of the series limit of the Balmer series.

a. $\nu_1 - \nu_2 = \nu_3$ b. $\nu_2 - \nu_1 = \nu_3$

c. $\nu_2 = \frac{1}{2}(\nu_1 + \nu_3)$ d. $\nu_1 + \nu_2 = \nu_3$

Sol.

a. Lyman series limit: ($n_1 = 1, n_2 = \infty$) ($\bar{\nu} \propto \nu$)

$$\nu_1 = RZ^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = RZ^2 = R(Z=1)$$

First line of Lyman ($n_1 = 1, n_2 = 2$)

$$\nu_2 = R \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4}R = \frac{3}{4}(\nu_1) \quad (\nu_1 = R)$$

Balmer series limit: ($n_1 = 1, n_2 = \infty$)

$$\nu_3 = R \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) = \frac{R}{4} = \frac{\nu_1}{4}$$

$$\nu_3 = (\nu_1 - \nu_2) = \left(\nu_1 - \frac{3}{4}\nu_1 \right) = \frac{\nu_1}{4}$$

$$\therefore (\nu_1 - \nu_2) = \nu_3$$

ILLUSTRATION 4.68

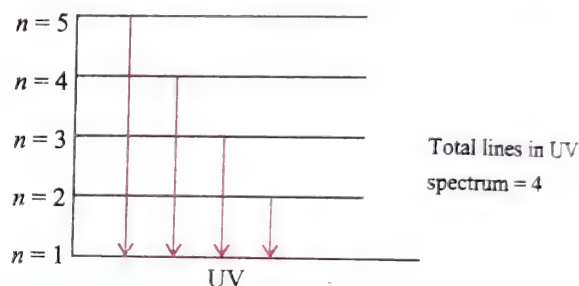
A certain transition in H spectrum from an excited state to the ground state in one or more steps gives rise to a total of 10 lines. How many of these belong to the UV spectrum?

- a. 3 b. 4 c. 6 d. 5

Sol.

b. $\frac{n(n-1)}{2} = 10, \therefore n = 5$

$n_1 = 1$ (ground state) $n_2 = 5$ (excited state)

**ILLUSTRATION 4.69**

The transition from state $n = 4$ to $n = 3$ in a He^{\oplus} ion result in ultraviolet radiation. Infrared radiation will be obtained in the transition from

- a. $n = 2 \rightarrow n = 1$ b. $n = 3 \rightarrow n = 2$
c. $n = 5 \rightarrow n = 4$ d. $n = 8 \rightarrow n = 6$

Sol.

d. In case of H-spectrum UV spectrum appears from $n_1 = 1$, to $n_2 = 2, 3 \dots$

Here in case of He^{\oplus} spectrum UV spectrum is from n_1 to $n_2 = 4$.

$$\bar{\nu}_{UV} = RZ^2 \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = R \times 4 \left(\frac{1}{3^2} - \frac{1}{4^2} \right)$$

In case of H-spectrum IR appears from $n_1 = 3, n_2 = 4, 5, \dots$

$$\bar{\nu}_{IR} \text{ for } \text{H}_2^{\oplus} = R \times 1^2 \left(\frac{1}{3^2} - \frac{1}{4^2} \right) \quad \dots(i)$$

$$\bar{\nu}_{IR} \text{ for } \text{He}^{\oplus} = R \times 4 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left(\frac{4}{n_1^2} - \frac{4}{n_2^2} \right) \quad \dots(ii)$$

Comparing the coefficients of equations (i) and (ii), we get

$$\frac{4}{n_1^2} = \frac{1}{9}; \quad n_1 = 6$$

$$\frac{4}{n_2^2} = \frac{1}{16}; \quad n_2 = 8$$

Thus, transition for He^{\oplus} in IR is $n_1 \rightarrow 6$ to $n_2 \rightarrow 8$.

Note: IR region starts with $n_1 = 3$.

ILLUSTRATION 4.70

An electron jumps from n th level to the first level. The correct fact(s) about H atoms is/are

- Number of spectral lines = $\frac{n(n-1)}{2}$
- If $n = 4$, number of spectral lines = 6
- Number of spectral lines = $\frac{n(n+1)}{2}$
- If $n = 4$, number of spectral lines = 10

Sol.

- Correct.
- Correct $\frac{4(4-1)}{2} = 6$
- and d. are wrong.

ILLUSTRATION 4.71

The electron of H-atom in the ground state is excited to a higher energy level by monochromatic light of energy 13.22 eV. How many different photons are emitted when it returns to the ground state?

- 4
- 10
- 6
- 15

Sol.

$$\text{d. } 13.22 \text{ eV} = 13.6 \left[\frac{1}{1^2} - \frac{1}{n^2} \right] = 13.6 - \frac{13.6}{n^2}$$

$$\frac{13.6}{n^2} = 13.6 - 13.22 = 0.38$$

$$n^2 = \frac{13.6}{0.38} \approx 36$$

$$n = 6.$$

The electrons of H atom is excited from $n_1 \rightarrow 1$ to $n_2 \rightarrow 6$.

$$\text{Number of spectral line} = \frac{6(6-1)}{2} = 15$$

The number of photons emitted is equal to the number of spectral lines = 15.

ILLUSTRATION 4.72

Ratio of frequency of revolution of electron in the second excited state of He^{\oplus} and second state of hydrogen is

- $\frac{32}{27}$
- $\frac{27}{32}$
- $\frac{1}{54}$
- $\frac{27}{2}$

Sol.

$$\text{a. Frequency } \nu = \frac{V}{2\pi r}; \quad V \propto \frac{Z}{n} \text{ and } r \propto \frac{n^2}{Z}$$

$$V = \frac{Z \times Z}{n \times n^2}$$

$$\Rightarrow \nu \propto \frac{Z^2}{n^3}$$

$$\text{So } \frac{\nu_{\text{He}^{\oplus}}}{\nu_{\text{H}_2^{\oplus}}} = \frac{2^2/3^3}{1^2/2^3} = \frac{8 \times 4}{27} = \frac{32}{27}$$

Second excited $\Rightarrow n = 3$.

ILLUSTRATION 4.73

The Wave length of the first line of Lyman series of hydrogen is identical to that of second line of Balmer series for same hydrogen like ion 'X'. The IE_2 for X is

- 54.4 eV
- 328 eV
- 13.6 eV
- 3.8 eV

Sol.

c.

$$\text{Given } \lambda(\text{Lyman}, \text{H}_2^{\oplus}) = \lambda(\text{Balmer}, \text{X})$$

$$\text{i.e. } R_H \times 1^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = R_H \cdot X^2 \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

Second line Balmer $\Rightarrow n = 4$.

$\Rightarrow X = 2$, Thus,

$$\text{IE}_2 = -13.6 \frac{Z^2}{n^2} = -13.6 \times \frac{2^2}{2^2} = -13.6 \text{ eV}$$

ILLUSTRATION 4.74

Which of the following is(are) correct for a H_2^{\oplus} like species?

- The energy gap between the consecutive energy orbits decreases as the value of " n " increases
- The longest wavelength in any spectral series corresponds to α -line in that series.
- Each spectral series is bounded by minimum and maximum wavelengths and the range follows a continuous distribution as given by Bohr's theory.
- Kinetic energy of the electron decreases, whereas the potential energy increases as the value of " n " increases.

Sol.

a., c., d.

a. Correct.

b. Wrong.

c. Correct statement.

$$\text{d. Correct. PE} \propto -\frac{1}{n^2} \quad \text{KE} \propto \frac{1}{n^2}$$

Therefore PE with proper sign will increase with increase in value of n whereas KE will decrease.

ILLUSTRATION 4.75

The ionisation energy of H atom is 13.6 eV. What will be the ionisation energy of He^{\oplus} and Li^{2+} ions?

Sol. Ionisation energy of H atom = 13.6 eV

$$\text{Ionisation energy of } \text{He}^{\oplus} = \text{IE for H} \times Z^2 \\ = 13.6 \times 4 = 54.4 \text{ eV}$$

$$\text{Ionisation energy for } \text{Li}^{2+} = \text{IE for H} \times Z^2 \\ = 13.6 \times 9 = 122.4 \text{ eV}$$

ILLUSTRATION 4.76

An electron in H atom jumps from the third energy level to the first energy level. The change in the potential energy of the electron is

- a. 12.09 eV b. 6.04 eV
c. 24.18 eV d. None

Sol. c. $\text{TE} = -\text{KE} = \frac{1}{2}\text{PE}$

$$\text{PE}_1 = 2\text{TE}_1 = 2 \times -13.6 \text{ eV} \\ = -27.2 \text{ eV (First orbit)}$$

$$\text{PE}_3 = 2\text{TE}_3 = 2 \times \frac{-13.6}{9} = \frac{-27.2}{9} \text{ eV}$$

$$\text{PE}_3 - \text{PE}_1 = \frac{-27.2}{9} - (-27.2) \\ = 27.2 \times \frac{8}{9} = 24.18 \text{ eV}$$

ILLUSTRATION 4.77

If the PE of an electron in the first Bohr orbit of H atom is zero, the total energy of the electron in second Bohr orbit is

- a. 23.8 eV b. -23.8 eV
c. -3.4 eV d. 3.4 eV

Sol. a. **In first orbit:**

TE = Total energy, KE = Kinetic energy, PE = Potential energy

$$\text{TE} = -13.6 = -\text{KE} = \frac{1}{2}\text{PE} \quad (\text{PE} = 2 \text{ TE})$$

$$\text{PE} = 2 \times -13.6 = -27.2$$

If PE = 0, add + 27.2 to PE.

$$\text{PE} = -27.2 + 27.2 = 0$$

$$\text{TE} = -13.6 + 27.2 = 13.6 \text{ eV}$$

$$\text{KE} = 13.6 + 27.2 = 40.8 \text{ eV}$$

In second orbit:

$$\text{TE} = \frac{-13.6}{4} = -3.4$$

$$= -3.4 + 27.2 = 23.8 \text{ eV}$$

$$\text{KE} = 3.4 + 27.2 = 30.6$$

ILLUSTRATION 4.78

- I. The circumference of the first Bohr orbit in H atom is $3.322 \times 10^{-10} \text{ m}$. What is the velocity of the electron of this orbit?

- II. The number of waves in the fourth Bohr orbit of hydrogen is

- a. 3 b. 4 c. 9 d. 12

- III. In hydrogen atoms, electrons are excited to the fifth energy level. The number of lines that may appear in the spectrum will be

- a. 4 b. 8 c. 10 d. 12

- IV. Calculate the radius of the third orbit of a hydrogen atom; the radius of the first Bohr orbit of hydrogen atom is 0.53 \AA .

- a. 4.77 \AA b. 1.59 \AA c. 1.06 \AA d. 2.12 \AA

Sol.

- I. According to Bohr's model,

$$mvr = \frac{nh}{2\pi}; \text{ Given } n = 1 \text{ and } 2\pi r \text{ (circumference)} \\ = 3.322 \times 10^{-10} \text{ m}$$

$$v = \frac{nh}{2\pi mr} = \frac{1 \times (6.626 \times 10^{-34} \text{ J s})}{(9.1 \times 10^{-31} \text{ kg}) \times 3.322 \times 10^{-10} \text{ m}} \\ = 2.19 \times 10^6 \text{ m s}^{-1}$$

- II. b. Number of waves = $\frac{\text{Circumference}}{\text{Wavelength}}$

$$\frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} = \frac{2\pi}{h} (mvr) = \frac{2\pi}{h} \times \frac{nh}{2\pi} = \frac{2\pi}{h} \times \frac{4h}{2\pi}$$

$$\therefore n = 4$$

- III. c. Number of lines produced for a jump from fifth orbit to first orbit is given by $n(n-1)/2$ required number of lines

$$= \frac{5(5-1)}{2} = 10$$

- IV. a. We know that

$$r_n = n^2 r_0 = (3)^2 \times 0.53 = 4.77 \text{ \AA}$$

ILLUSTRATION 4.79

- I. The energy of an electron in the first Bohr orbit of H atom is -13.6 eV . The possible energy value (s) of excited state(s) for the electron in the Bohr orbit of hydrogen is/are

- a. -3.4 eV b. -4.2 eV c. 6.8 eV d. $+6.8 \text{ eV}$

- II. If an electron in H atom has an energy of $-78.4 \text{ kcal mol}^{-1}$. The orbit in which the electron is present is

- a. 1st b. 2nd c. 3rd d. 4th

- III. If the radius of the second Bohr orbit of hydrogen atom is r_2 , the radius of the third Bohr orbit will be

- a. $\frac{4}{9} r_2$ b. $4r_2$ c. $\frac{9}{4} r_2$ d. $9r_2$

- IV. The difference between n th and $(n+1)$ th Bohr radius of H atom is equal to its $(n-1)$ th Bohr radius. The value of n is

- a. 1 b. 2 c. 3 d. 4

Sol.

I. a. $E_n = \frac{-13.6}{n^2} \text{ eV}$

When $n = 2$, $E_2 = \frac{-13.6}{4} = -3.4 \text{ eV}$

Hence, (a) is the correct answer.

II. b. $E_n = \frac{-313.6}{n^2} \text{ kcal mol}^{-1}$

$\Rightarrow -78.4 = \frac{-313.6}{n^2}$

$\therefore n = 2$

III. c. $r = \frac{n^2 h^2}{4\pi^2 m Z e^2}$

$\therefore \frac{r_2}{r_3} = \frac{2^2}{3^2}$

$\therefore r_3 = \frac{9}{4} r_2$

IV. d. $r_n \propto n^2$

But $r_{n+1} - r_n = r_{n-1}$

$(n+1)^2 - n^2 = (n-1)^2$

$n = 4$

ILLUSTRATION 4.80

I. Which of the following are the limitations of Bohr's model?

- It could not explain the intensities or the fine spectrum of the spectral lines.
- No justification was given for the principle of the quantization of angular momentum.
- It could not explain why atoms should combine to form bond.
- It could not be applied to multi-electron atoms.

II. According to Bohr's theory:

- When an atom gets the required energy from outside, it jumps from lower orbits to higher orbits and remains there
- When an atom gets the required energy from outside, it jumps from lower orbits to higher orbits and remains there for very short intervals of time and returns back to the lower orbit, radiating energy
- Angular momentum of an electron is proportional to n
- Angular momentum of an electron is independent of n

III. Choose the correct relations on the basis of Bohr's theory.

- Velocity of electron $\propto 1/n$
- Frequency of revolution $\propto 1/n^3$
- Radius of orbit $\propto n^2 Z$
- Force on electron $\propto 1/n^4$

Sol.

I. (a), (b), (c), (d) all.

II. (b) and (c).

III. (a) and (d).

ILLUSTRATION 4.81

I. Bohr's orbits are called stationary states because

- Electrons in them are stationary
- Their orbits have fixed radii
- The electrons in them have fixed energy
- The protons remain in the nuclei and are stationary

II. Which of the following statements is (are) correct in Bohr's model if the mass of an electron becomes 10 times its original mass?

- Velocity of the electron increases by 10 times.
- Orbit radius decreases by 10 times.
- Energy of the electron increases by 10 times.
- Wavelength of the electron will remain same.

III. The velocity of an electron in the second Bohr orbit of an atom of an element is $1.1 \times 10^6 \text{ m s}^{-1}$. Its velocity in the third orbit is

- $3.3 \times 10^6 \text{ m s}^{-1}$
- $2.2 \times 10^6 \text{ m s}^{-1}$
- $7.333 \times 10^5 \text{ m s}^{-1}$
- $3.66 \times 10^5 \text{ m s}^{-1}$

IV. If the radius of the Bohr orbit is r then the de Broglie wavelength of the electron in the third orbit will be

- $2\pi r$
- $\frac{2\pi r}{3}$
- $\frac{3\pi r}{3}$
- $6\pi r$

Sol.

I. c. The electrons in them have fixed energy.

II. d. Wavelength of the electron will remain same.

III. c. Let $V_1 = x \text{ ms}^{-1}$

$\therefore V_2 = -\frac{x}{2} \text{ ms}^{-1}$

$V_3 = \frac{x}{3} \text{ ms}^{-1}$

$\frac{x}{2} = 1.1 \times 10^6 \text{ ms}^{-1} \text{ (Given)}$

$\therefore x = 2.2 \times 10^6 \text{ ms}^{-1}$

$V_3 = \frac{2.2 \times 10^6 \text{ ms}^{-1}}{3}$
 $= 7.333 \times 10^5 \text{ m s}^{-1}$

IV. b. Bohr radius = r

Bohr velocity, $V = \frac{nh}{2\pi mr}$

de-Broglie wavelength, $\lambda = \frac{h}{mv}$

\therefore For third orbit, $n = 3$

$\therefore \lambda = \frac{h}{m \times 3V} = \frac{2\pi r}{3}$
 $\frac{h}{2\pi mr}$

ILLUSTRATION 4.82

I. Which of the following statements does not form part of Bohr's model of the hydrogen atom?

- a. Energy of the electron in the orbit is quantized.
 b. The electron in the orbit nearest to the nucleus has the lowest energy.
 c. Electrons revolving in different orbits have different velocities.
 d. The position and velocity of the electron in the orbit cannot be determined simultaneously.
- II. If the speed of electron in the first Bohr orbit of hydrogen atom is x , then the speed of the electron in the third Bohr orbit of hydrogen is
- a. $\frac{x^2}{9}$ b. $\frac{x}{3}$ c. $3x$ d. $9x$
- III. The ratio of the difference between the first and second Bohr orbit energies to that between second and third Bohr orbit energies is
- a. $\frac{1}{2}$ b. $\frac{1}{3}$ c. $\frac{27}{5}$ d. $\frac{5}{27}$
- IV. Which of the following parameters are not same for all hydrogen-like atoms and ions in their ground state?
- a. Radius of orbit
 b. Speed of electron
 c. Energy of the atom
 d. Orbital angular momentum of electron

Sol.

I. d.

II. b. Velocity, $V \propto \frac{Z}{n}$

If velocity of electron in first orbit = x
 then velocity in 3rd orbit = $\frac{x}{3}$

III. c. $\Delta E = -2.18 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ J atom}^{-1}$

$$\therefore \Delta E_{2 \rightarrow 1} = -2.18 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$= -2.18 \times 10^{-18} \left(\frac{3}{4} \right)$$

$$\therefore \Delta E_{3 \rightarrow 2} = -2.18 \times 10^{-18} \left(\frac{5}{36} \right)$$

$$\therefore \frac{\Delta E_{2 \rightarrow 1}}{\Delta E_{3 \rightarrow 2}} = \frac{3}{4} \times \frac{36}{5} = \frac{27}{5}$$

Hence answer is (c)

IV. (a, b, c)

ILLUSTRATION 4.83

I. If the radius of first, second, third and fourth orbits of hydrogen atom are r_1, r_2, r_3 , and r_4 , respectively, then their correct increasing order will be

a. $r_4 < r_3 < r_2 < r_1$

b. $r_1 < r_2 < r_3 < r_4$

c. $r_1 < r_2 > r_3 > r_4$

d. Equal in all

II. The ratio of the radii of the fifth orbits of He^{\oplus} and Li^{\oplus} will be

a. 2 : 3

b. 3 : 2

c. 4 : 1

d. 5 : 3

III. Which of the following orbits of hydrogen atom should have the values of their radii in the ratio of 1:4?

a. K and L

b. L and N

c. M and N

d. (a) and (b) are correct

IV. If $a = \frac{h}{4\pi^2 m e^2}$, then the correct expression for calculation of the circumference of the first orbit of hydrogen atom is

a. $\sqrt{4h^2} \pi a$

b. $2\pi r$

c. $\sqrt{4} \pi h a$

d. (a) and (c) are correct

Sol.

I. c. $r \propto n^2$

$$\therefore r_1 < r_2 < r_3 < r_4$$

II. b. Here n is a constant, therefore

$$\frac{r_1}{r_2} = \frac{Z_2}{Z_1} = \frac{3}{2} = 3:2$$

III. d. a. Ratio of radii of orbits K and L

$$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2} = \frac{1^2}{2^2} = 1:4$$

b. Ratio of radii of orbits L and N

$$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2} = \frac{2^2}{4^2} = 4:16 \text{ or } 1:4$$

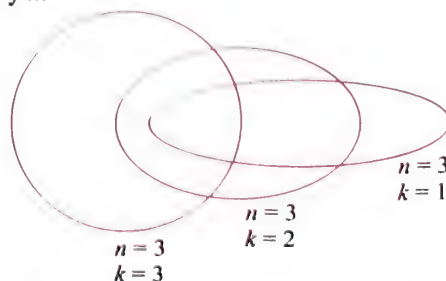
IV. d. Circumference = $2\pi r$

$$2 \times \pi \times \frac{n^2 h^2}{4\pi^2 m Z e^2}, n=1, Z=1 \text{ and } \frac{h}{4\pi^2 m e^2} = a$$

$$\text{Thus } 2 \times \pi \times h \times a \text{ or } \sqrt{4\pi h a} \text{ or } \sqrt{4h^2} \pi a$$

4.25 BOHR-SOMMERFELD'S ATOMIC THEORY

When atomic spectrum was studied using high resolution spectrographs, each line was found to consist of a number of closely spaced lines. This finer structure of spectrum could not be explained on the basis of Bohr's concept of circular orbits. Sommerfeld in 1915 extended Bohr's model by proposing that electrons in an atom have elliptical orbits. An ellipse has a major axis and a minor axis. A circle is a special case of ellipse where the major and the minor axes are of the same length. In order to represent the motion of an electron in elliptical orbit, two quantum numbers are needed in place of one employed by Bohr. This new quantum number has been called azimuthal quantum number and is denoted by k .

Fig. 4.21 Bohr-Sommerfeld orbits for $n = 3$

The principal quantum number n determines the length of the major axis, and the azimuthal quantum number k determines the length of the minor axis. It can be shown that

$$\frac{n}{k} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

The possible values of k range from 1 to n ; all are integral values. Thus, when $n = 3$, $k = 1, 2$, and 3 . When $n = k$, the orbit is circular. Thus, for the third energy level, three orbits are possible, one circular and two elliptical, as shown in Fig. 4.21.

Applying the principle of quantization of momentum to the electron moving in an elliptical orbit, Sommerfeld deduced the energy of the electron in the hydrogen atom as

$$E_n = -\frac{2\pi^2 e^4 m}{(n+k)^2 h^2}$$

Thus, we find that the energy depends not only on the principal quantum number n but also on the azimuthal quantum number k . The frequency of the radiation emitted as a result of transition of an electron from a level of energy E_2 to a level of energy E_1 ($E_2 < E_1$) would, therefore, vary depending on the various values of k , and as a result, a group of closely spaced lines would appear instead of a single line in the spectrum of hydrogen atom or hydrogen-like atoms.

The concept of Sommerfeld postulates the existence of sub-energy level for electron in each of the principal energy levels of the atom.

4.25.1 DRAWBACKS OF SOMMERFELD'S MODEL

Experimental observation and theoretical treatment based wave mechanics show that the different values of azimuthal quantum number are: $0, 1, 2, 3, \dots, (n-2), (n-1)$ (total n values) and not $1, 2, 3, \dots, (n-1), n$. The new quantum number beginning with zero and ending at $(n-1)$ has been represented by l . Thus l and k are related as: $l = k - 1$ and $l = 0, 1, 2, \dots, (n-1)$.

Sommerfeld's theory cannot give the correct number of lines observed in the fine structure. Moreover, it gives no information about the relative intensities of the 'five lines'. Further, the exact definition of position and momentum is contrary to the uncertainty principle.

4.26 DUAL BEHAVIOUR OF MATTER

In order to overcome the shortcomings of Bohr's model, several attempts were made to develop a more suitable and general model for atoms. Louis de Broglie in 1929 and Heisenberg in 1927 gave two important theories which contributed significantly to the formulation of such a model.

In 1924, a French physicist Louis de Broglie proposed that matter, like radiation, should also exhibit dual behaviour, i.e., both particle and wave-like properties. This means that just as the photon has momentum as well as wavelength, electrons must also have momentum as well as wavelength. According to de Broglie, the wavelength λ of an electron is inversely proportional to the momentum (P) of a material particle.

$$\lambda \propto \frac{1}{P} \quad \text{or} \quad \lambda = \frac{h}{P} = \frac{h}{mv}$$

where h = Planck's constant; m = mass of the particle, v = velocity, and P = Momentum.

4.26.1 RELATION OF DE BROGLIE WAVELENGTH (λ) WITH KINETIC ENERGY (E) OF THE PARTICLE

It is mentioned here that wavelength of the de Broglie wave can also be related to the kinetic energy (E) of the particle.

$$E = \frac{1}{2} mv^2 \quad \dots(i)$$

$$mE = \frac{1}{2} m^2 v^2 \quad \dots(ii)$$

$$m^2 v^2 = 2mE \quad \dots(iii)$$

$$\text{or } mv = (2mE)^{1/2}$$

Substituting this value of mv in de Broglie equation, we get

$$\lambda = \frac{h}{mv} = \frac{h}{(2mE)^{1/2}} \quad \dots(iv)$$

If a charged particle carrying charge Q coulomb is accelerated by applying a potential difference of V volt, then the kinetic energy of the particle is given by the relation

$$E = (Q \times V) \text{ J}$$

Substituting this expression in expression (iv), we get

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{h}{(2mQV)^{1/2}} \quad \dots(v)$$

4.26.2 DIFFERENCE BETWEEN ELECTROMAGNETIC WAVES AND MATTER WAVES

The waves associated with material particles or objects in motion are called matter waves or de Broglie waves. The matter waves are significantly different from electromagnetic waves. The main differences are listed in Table 4.8.

Table 4.8 Difference between electromagnetic waves and matter waves

	Electromagnetic waves		Matter waves
a.	These waves are associated with electrical and magnetic fields.	a.	These waves are not associated with any field.
b.	These waves can be emitted or radiated in space.	b.	Matter waves are neither radiated into space nor emitted by the particle. These are associated with the particle.
c.	All electromagnetic waves travel with the speed of light ($3.0 \times 10^8 \text{ m s}^{-1}$).	c.	The velocity of matter waves is different from that of light and all matter waves travel with different velocities.
d.	The wavelength of electromagnetic waves is given by $\lambda = \frac{c}{\nu} = \frac{h}{mc}$	d.	The wavelength of matter waves is given by $\lambda = \frac{h}{mv} = \frac{h}{P}$

4.26.3 SIGNIFICANCE OF DE BROGLIE WAVES

Unlike particles, waves do not occupy a well-defined position in space and are delocalised; hence, the wave character puts some

restrictions on precisely expressing the position of an electron or other small moving particles. According to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short because of their large masses that their wave properties cannot be detected.

For example, a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} has a wavelength of $6.626 \times 10^{-34} \text{ m}$. It is too small to be detected. Therefore, such bodies have predominantly particle character. The wavelengths associated with electrons and other subatomic particles with very small masses are associated with observable length and can be detected experimentally. For example, an electron moving with a velocity of $6.0 \times 10^6 \text{ m s}^{-1}$ is associated with a wave of wavelength $1.21 \times 10^{-10} \text{ m}$ or 121 pm.

4.26.4 EXPERIMENTAL VERIFICATION OF THE DUAL CHARACTER OF ELECTRONS

a. Verification of wave character

i. **Davisson and Germer's experiment:** Davisson and Germer in 1927 observed that when a beam of electrons is allowed to fall on the surface of a nickel crystal and the scattered or the reflected rays are received on a photographic plate, a diffraction pattern (consisting of a number of concentric rings) similar to that produced by X-rays is obtained. Now, since X-rays are electromagnetic waves, i.e., they are confirmed to have wave character, electrons must also have wave character. Moreover, the wavelength determined from the diffraction pattern is found to be very nearly the same as calculated from de Broglie equation. This further lent support to the de Broglie equation.

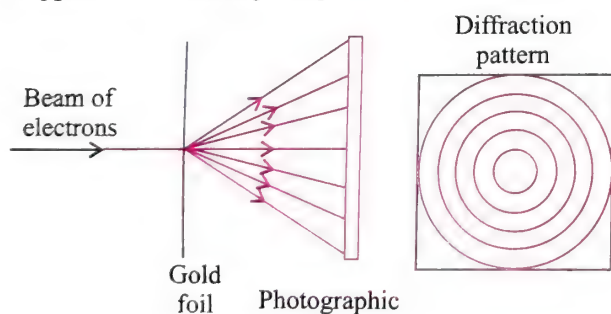


Fig. 4.22 Electron diffraction experiment by Davisson and Germer

ii. **Thomson's experiment:** G.P. Thomson in 1928 performed experiments with a thin foil of gold in place of nickel crystal. He observed that if the beam of electrons, after passing through the thin foil of gold, is received on the photographic plate placed perpendicular to the direction of the beam, a diffraction pattern is observed as before. This again confirmed the wave nature of electrons.

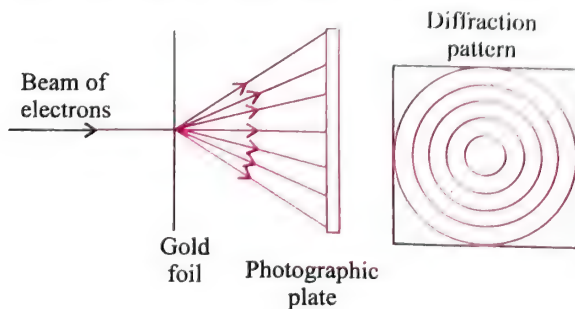


Fig. 4.23 Thomson experiment

b. **Verification of the particle character:** The particle character of electrons is proved by the fact that when an electron strikes a zinc sulphide screen, a spot of light, known as scintillation, is produced.

Since scintillation is localised on the zinc sulphide screen, the striking electron that produces it also must be localised and is not spread out on the screen. But the localised character is possessed by particles. Hence, electrons have particle character.

Further experiments such as Thomson's experiment for determination of the ratio of charge and mass (i.e., e/m), **Millikan oil drop experiment** for determination of charge on electron and **black body radiation** also show that electrons have particle character.

The most important application of de Broglie concept is in the construction of electron microscope, which is used in the measurement of objects of very small size.

4.26.5 DERIVATION OF BOHR'S POSTULATE OF ANGULAR MOMENTUM FROM DE BROGLIE EQUATION

According to Bohr's model, an electron revolves around the nucleus in circular orbits. According to de Broglie concept, the electron is not only a particle but also has a wave character. Thus in order that the wave may be completely in phase (Fig. 4.24), the circumference of the orbit must be equal to an integral multiple of wavelength (λ), i.e., $2\pi r = n\lambda$, where r is the radius of the orbit and n is an integer.

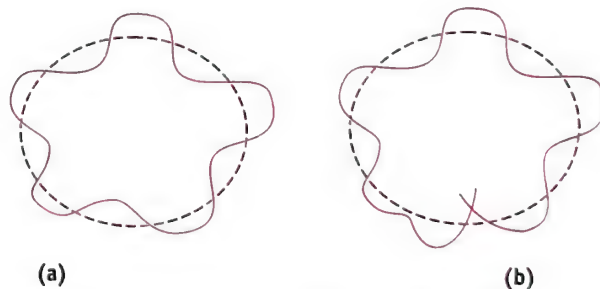


Fig. 4.24 Wave (a) in and (b) out of phase

$$\text{But } \lambda = \frac{h}{mv} \text{ (de Broglie equation)}$$

$$\text{or } mvr = n \frac{h}{2\pi}$$

which is Bohr's postulate of angular momentum

4.27 HEISENBERG'S UNCERTAINTY PRINCIPLE

For macroscopic objects, both the position and velocity can be determined accurately at any instance. Hence, the paths or trajectories of such bodies can be predicted precisely. However, such an accurate measurement is not possible for subatomic particles such as electrons. Hence, it is not possible to talk of trajectory of an electron. Werner Heisenberg, a German physicist, in 1927 put forward this fact known as Heisenberg's uncertainty principle.

This principle is a direct consequence of dual behaviour of matter and radiation. It states that it is impossible to determine simultaneously the exact position and exact momentum (or velocity) of an electron.

Mathematically, it can be given as:

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\text{or } \Delta x \times \Delta(mv) \geq \frac{h}{4\pi}$$

$$\text{or } \Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

where Δx is the uncertainty in position and Δp (or Δv) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with a high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain (Δv is large).

4.27.1 EXPLANATION OF HEISENBERG'S UNCERTAINTY PRINCIPLE

The basis for the above principle may be understood from the following discussion:

Suppose we attempt to measure both the position and momentum of an electron. To pinpoint the position of the electron, we have to use light so that a photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the hitting, the position, as well as the velocity, of the electron is disturbed.

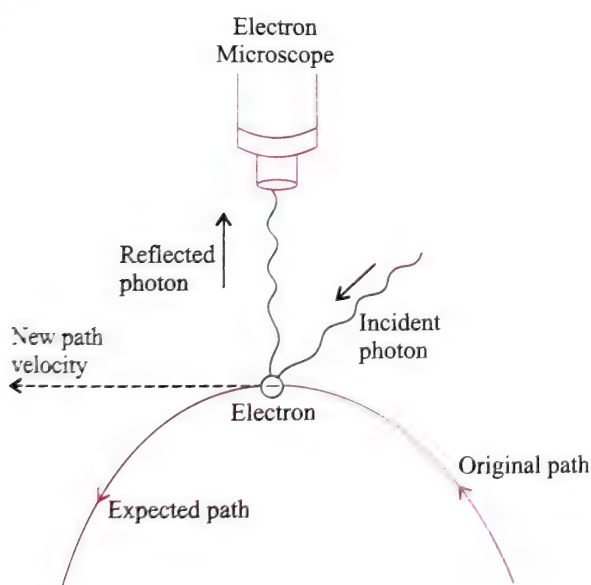


Fig. 4.25 The change in the path of electron by a photon of light

But according to the principle of optics, the accuracy with which the position of a particle can be measured depends upon the wavelength of light used. The uncertainty in position is $\pm \lambda$. The shorter the wavelength, the greater the accuracy. But shorter wavelength means higher frequency and, hence, higher energy. This high energy photon, on striking the electron, changes its speed as well as direction.

Alternatively, shorter wavelength implies higher momentum (as $\lambda = h/p$, i.e., $p = h/\lambda$). Thus, photon will have a higher

momentum, and a larger but indefinite amount of it will be transferred to the electron at the time of collision. This will result in a greater uncertainty in the velocity of the electron. On the other hand, decreasing the momentum means increasing the wavelength, which will lead to a greater uncertainty in position.

4.27.2 SIGNIFICANCE OF UNCERTAINTY PRINCIPLE

One of the important implications of the Heisenberg uncertainty principle is that it rules out the existence of definite paths or trajectories of electrons and other similar particles. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be some time later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a subatomic object such as an electron it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk about the trajectory about an electron.

The effect of Heisenberg uncertainty principle is significant only for the motion of microscopic objects and is negligible for that of macroscopic objects. This may be illustrated in the following examples.

If the uncertainty principle is applied to an object of mass say about a milligram (10^{-6} kg), then

$$\Delta v \times \Delta x = \frac{h}{4\pi m} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.1416 \times 10^{-6} \text{ kg}} \approx 10^{-28} \text{ m}^2 \text{ s}^{-1}$$

The value of $\Delta v \times \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.

In case of a microscopic object like an electron $\Delta v \cdot \Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg, according to Heisenberg uncertainty principle

$$\Delta v \cdot \Delta x = \frac{h}{4\pi m} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 9.11 \times 10^{-31}} \approx 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

The value is quite large and cannot be neglected. For example, if the uncertainty in position of the electron is 10^{-8} m, then the uncertainty Δv in velocity will be

$$\frac{10^{-4} \text{ m}^2 \text{ s}^{-1}}{10^{-8} \text{ m}} \approx 10^4 \text{ m s}^{-1}$$

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by statements of probability that the electron has at a given position and momentum.

4.27.3 WHY ELECTRON DOES NOT EXIST IN NUCLEUS

The radius of the nucleus is of the order of 10^{-13} cm, and thus, the uncertainty in position of the electron, (i.e., Δx), if it is within the nucleus, will be 10^{-13} cm.

$$\text{Now } \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

$$\therefore \Delta v = \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 9.108 \times 10^{-28} \times 10^{-13}} \\ = 5.79 \times 10^{12} \text{ cm s}^{-1}$$

i.e., the order of velocity of the electron will be 100 times greater than the velocity of light, which is impossible. Thus, possibility of the electron to exist in the nucleus is zero.

4.28 REASON FOR THE FAILURE OF THE BOHR MODEL

After the success of the de Broglie principle of wave-particle duality of an electron and Heisenberg uncertainty principle, the Bohr model was completely disregarded because in this model, the wave character of the electron is not considered and it also contradicts Heisenberg uncertainty principle. In the Bohr model, an orbit is a clearly defined path, which means that both the position and the velocity of the electron are known exactly at the same time, which contradicts Heisenberg uncertainty principle.

ILLUSTRATION 4.84

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 ms^{-1} ?

Sol. $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(0.1 \text{ kg})(10 \text{ ms}^{-1})}$
 $= 6.626 \times 10^{-34} \text{ m} \quad (J = \text{kg m}^2 \text{ s}^{-2})$

ILLUSTRATION 4.85

The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. If its K.E. is $3.0 \times 10^{-25} \text{ J}$. Calculate its wavelength

Sol. Since K.E. = $\frac{1}{2}mv^2$

$$\therefore v = \left(\frac{2 \text{ K.E.}}{m} \right)^{\frac{1}{2}} = \left(\frac{2 \times 3.0 \times 10^{-25} \text{ kg} \cdot \text{m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \right)^{\frac{1}{2}}$$

$$= 812 \text{ ms}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(812 \text{ ms}^{-1})}$$

$$= 8967 \times 10^{-10} \text{ m} = 896.7 \text{ nm}$$

ILLUSTRATION 4.86

Calculate the mass of a photon with wavelength 3.6 \AA .

Sol. $\lambda = 3.6 \text{ \AA} = 3.6 \times 10^{-10} \text{ m}$

Velocity of photon = Velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34} \text{ Js}}{(3.6 \times 10^{-10} \text{ m})(3 \times 10^8 \text{ ms}^{-1})}$$

$$= 6.135 \times 10^{-29} \text{ kg}$$

ILLUSTRATION 4.87

What is the ratio of the velocities of CH_4 and O_2 molecules so that they are associated with de Broglie waves of equal wavelength?

Sol. From the de Broglie relationship

$$\lambda = \frac{h}{mv}$$

For CH_4 , $\lambda_{\text{CH}_4} = \frac{h}{m_{\text{CH}_4} \times v_{\text{CH}_4}} \quad \dots(i)$

For O_2 , $\lambda_{\text{O}_2} = \frac{h}{m_{\text{O}_2} \times v_{\text{O}_2}} \quad \dots(ii)$

Wavelength of CH_4 and O_2 is equal, hence

$$\frac{h}{m_{\text{CH}_4} \times v_{\text{CH}_4}} = \frac{h}{m_{\text{O}_2} \times v_{\text{O}_2}}$$

$$\Rightarrow \frac{v_{\text{CH}_4}}{v_{\text{O}_2}} = \frac{m_{\text{O}_2}}{m_{\text{CH}_4}} = \frac{32}{16} = 2$$

$$\therefore v_{\text{CH}_4} = 2 v_{\text{O}_2}$$

The velocity of CH_4 molecule is two times the velocity of O_2 molecule.

ILLUSTRATION 4.88

Which of the following is associated with a de Broglie wave of longer wavelength—a proton or an electron having same velocity?

Sol. The wavelength of the de Broglie wave associated with a particle is inversely proportional to the mass of the particle. Since the mass of electron is less than that of proton, wavelength of the de Broglie waves associated with the electron will be more.

ILLUSTRATION 4.89

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 \AA . What is the uncertainty involved in the measurement of its velocity?

Sol. $\Delta x \times \Delta p = \frac{h}{4\pi}$

or $\Delta x \times m\Delta v = \frac{h}{4\pi}$

$$\Delta v = \frac{h}{4\pi \times \Delta x \times m}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 1 \times 10^{-10} \text{ m} \times 9.11 \times 10^{-31} \text{ kg}}$$

$$= 0.579 \times 10^7 \text{ ms}^{-1} \quad (1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2})$$

$$= 5.79 \times 10^6 \text{ ms}^{-1}$$

ILLUSTRATION 4.90

A golf ball has a mass of 40 g and a speed of 45 m s^{-1} . If the speed can be measured with an accuracy of 2% , calculate the uncertainty in the position.

Sol. Mass of the ball = 40 g = 40×10^{-3} kg
The uncertainty in the speed

$$\Delta v = 45 \times \frac{2}{100} = 0.9 \text{ m s}^{-1}$$

So the uncertainty in position

$$\begin{aligned}\Delta x &= \frac{h}{4\pi \Delta p} = \frac{h}{4\pi m \Delta v} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times (40 \times 10^{-3} \text{ kg}) \times (0.9 \text{ m s}^{-1})} \\ &= 1.46 \times 10^{-33} \text{ m}\end{aligned}$$

ILLUSTRATION 4.91

What is the minimum product of the uncertainty in position and the uncertainty in momentum of a moving electron?

Sol. The minimum product of two uncertainties is equal to $h/4\pi$.

ILLUSTRATION 4.92

If the uncertainty in the position of a moving electron is equal to its de Broglie wavelength, then its velocity will be completely uncertain. Explain.

Sol. Given that the uncertainty in position (Δx) is equal to de Broglie wavelength (λ), i.e., $\Delta x = \lambda$.

But according to de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

$$\text{or } \Delta x = \frac{h}{p} \quad (\text{Given condition})$$

According to Heisenberg uncertainty principle,

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

$$\left(\frac{h}{p}\right) \Delta p \geq \frac{h}{4\pi}$$

$$\frac{\Delta p}{p} \geq \frac{h}{4\pi \times h}$$

$$\frac{\Delta p}{p} \geq \frac{1}{4\pi} \quad (\text{constant})$$

$$\frac{\Delta v}{v} \geq \frac{1}{4\pi}$$

$$v \leq \Delta v \times 4\pi$$

ILLUSTRATION 4.93

I. An electron with velocity v is found to have a certain value of de Broglie wavelength. The velocity that the neutron should possess to have the same de Broglie wavelength is

- a. v b. $v/1840$
c. $1840v$ d. $1840/v$

II. The mathematical expression for the uncertainty principle is

$$\text{a. } \Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\text{c. } \Delta x \Delta p \geq \frac{h}{p}$$

$$\text{b. } \Delta E \Delta t \geq \frac{h}{4\pi}$$

$$\text{d. } \Delta E \Delta t \geq \frac{h}{p}$$

Sol.

$$\text{I. b. } \lambda_e = \frac{h}{m_e v_e}$$

$$\lambda_n = \frac{h}{m_n v_n}$$

$$\frac{h}{m_e v_e} = \frac{h}{m_n v_n}$$

$$v_n = \frac{m_e v_e}{m_n} = \frac{1}{1840} \times v_e \quad \left(m_e = \frac{1}{1840} m_n\right)$$

II. (a, b)

$$\text{a. } \Delta x \Delta p \geq \frac{h}{4\pi}$$

b. We know that

$$\Delta E = m \Delta V^2 = m \left(\frac{\Delta x}{\Delta t}\right)^2$$

$$\text{or } \Delta E \cdot \Delta t = m \frac{\Delta x^2}{\Delta t} \quad \dots(i)$$

$$\Delta x \Delta p > \frac{h}{4\pi}$$

$$\text{or } \Delta x m \Delta V \geq \frac{h}{4\pi}$$

$$\Rightarrow \Delta x m \frac{\Delta x}{\Delta t} \geq \frac{h}{4\pi}$$

$$\Rightarrow m \frac{\Delta x^2}{\Delta t} \geq \frac{h}{4\pi} \quad \dots(ii)$$

On comparing (i) and (ii), we get

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

ILLUSTRATION 4.94

An electron is accelerated through a potential difference of V volts. Find the de Broglie wavelength associated with the electron.

Sol. When the electron is accelerated through a potential difference of V volts, it acquires a kinetic energy given by $E = qV$, where q is the charge on the electron. Also, if m is its mass and v is its velocity, then

$$E = \frac{1}{2} m v^2$$

$$\Rightarrow v = \sqrt{\frac{2E}{m}}$$

And de Broglie wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2Em}}$$

ILLUSTRATION 4.95

Calculate the retarding potential to be applied to an electron to increase its de Broglie wavelength from 1.75 Å to 2.25 Å?

Sol. Wavelength change = $2.25 - 1.75 = 0.5$ Å

$$\text{Energy decrease} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m s}^{-1}}{0.5 \times 10^{-10} \text{ m}} = 3.975 \times 10^{-15} \text{ J}$$

$$eV_0 = E \\ (1.6 \times 10^{-19} \text{ C})V_0 = 3.975 \times 10^{-15}$$

$$V_0 = \frac{3.975 \times 10^{-15}}{1.6 \times 10^{-19}} = 24843.75 \text{ Volt}$$

It looks very much logical to do in this way. But the mistake here is that $\lambda = c/\nu$ is applicable to only electromagnetic waves and not particle waves. The correct method is as follows:

$$\begin{aligned} \Delta E &= \frac{1}{2} m (\nu_1^2 - \nu_2^2) \\ &= \frac{1}{2} \left[\left(\frac{h}{m\lambda_1} \right)^2 - \left(\frac{h}{m\lambda_2} \right)^2 \right] \\ &= \frac{1}{2} m \frac{h^2}{m^2} \left[\left(\frac{1}{\lambda_1} \right)^2 - \left(\frac{1}{\lambda_2} \right)^2 \right] = \frac{h^2}{2m} [0.1289 \times 10^{19}] \end{aligned}$$

$$eV_0 = \Delta E$$

$$V_0 = \frac{\Delta E}{e} = \frac{(6.626 \times 10^{-34} \text{ Js})^2 \times (0.1289 \times 10^{19} \text{ m}^{-2})}{(2 \times 9.1 \times 10^{-31} \text{ kg}) (1.6 \times 10^{-19} \text{ C})} = 1.943 \text{ Volt}$$

ILLUSTRATION 4.96

Calculate the uncertainty in the position (Δx) of an electron if Δv is 0.1%. Take the velocity of electron = $2.2 \times 10^6 \text{ m s}^{-1}$ and mass of electron as $9.108 \times 10^{-31} \text{ kg}$.

Sol. Given, $\Delta v = 0.1\%$ of the velocity of the electron

$$= \frac{0.1}{100} \times 2.2 \times 10^6 = 2.2 \times 10^3 \text{ m s}^{-1}$$

$$\Delta x \cdot m \Delta v = \frac{h}{4\pi}$$

$$\begin{aligned} \text{or } \Delta x &= \frac{6.63 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 9.108 \times 10^{-31} \text{ kg} \times 2.2 \times 10^3 \text{ m s}^{-1}} \\ &= 0.02624765 \times 10^{-6} \text{ m} \\ &= 262.4765 \times 10^{-10} \text{ m} \end{aligned}$$

Since Δx is much longer than the atomic diameter ($\approx 10^{-10} \text{ m}$), the uncertainty principle is applicable in this case.

ILLUSTRATION 4.97

I. If a light of wavelength λ hits the moving electron, the uncertainty in measurement of its position will be

- a. Greater than λ b. Less than λ
c. Equal to λ d. Any value

II. If the uncertainty in the position of an electron is zero, the uncertainty in its momentum be

- a. Zero b. $\frac{h}{2\pi}$ c. $\frac{h}{4\pi}$ d. Infinity

III. If E_1 , E_2 , and E_3 represent respectively, the kinetic energies of an electron, an alpha particle, and a proton each having same de Broglie wavelength, then

- a. $E_1 > E_3 > E_2$ b. $E_2 > E_3 > E_1$
c. $E_1 < E_3 < E_2$ d. $E_1 = E_2 = E_3$

IV. The uncertainty in position of an electron is equal to its de Broglie wavelength. The minimum percentage error in its measurement of velocity under this circumstance will be approximately

- a. 4 b. 8 c. 22 d. 18

V. If the energy of a photon of frequency ν is given by $E = h\nu$ where h is Planck's constant and the momentum of photon is $p = h/\lambda$, where λ is the wavelength of photon, then the velocity of light is equal to:

- a. $\sqrt{\frac{E}{p}}$ b. $\frac{E}{p}$ c. $E \times p$ d. $\left(\frac{E}{p}\right)^2$

VI. An electron is continuously accelerated in vacuum tube by applying potential difference. If its de Broglie wavelength is decreased by 1%, the change in the kinetic energy of the electron is nearly

- a. Decreased by 1.0% b. Increased by 2.0%
c. Increased by 1.0% d. Decreased by 2.0%

Sol.

I. c. Equal to λ

II. d. Infinity

III. a. $E_1 > E_3 > E_2$

$$\text{K.E} \propto \frac{1}{\text{Mass of particle}}$$

IV. b. de Broglie wavelength (λ) = $\frac{h}{p}$

$$\text{or } \Delta x \text{ (uncertainty in position)} = \frac{h}{p}$$

$$\therefore \Delta x \cdot \Delta p = \frac{h}{4\pi}$$

$$\text{or } \frac{h}{p} \times \Delta p = \frac{h}{4\pi}$$

$$\frac{\Delta p}{p} = \frac{1}{4\pi}$$

$$\text{or } \frac{m \times \Delta v}{m \times v} = \frac{1}{4\pi}$$

$$\text{or } \frac{\Delta v}{v} = \frac{1}{4\pi}$$

$$\therefore \% \text{ (uncertainty in velocity)} = \frac{\Delta v}{v} \times 100 = \frac{1}{4\pi} \times 100 \approx 8\%$$

V. b. Given $E = h\nu$ or $\frac{h\nu}{\lambda}$... (1)

$$\text{but } \lambda = \frac{h}{p} \text{ (given)} \dots (2)$$

Substituting equation (2) in (1), we get

$$E = \frac{h\nu}{h/p} = v \times p$$

$$\text{or } v (\text{velocity}) = \frac{E}{p}$$

$$\text{VI. b. } \lambda \propto \frac{1}{\sqrt{KE}} = \frac{\lambda_1}{\sqrt{KE_1}} = \frac{\lambda_2}{\sqrt{KE_2}} \text{ or } \frac{\lambda_1}{0.99\lambda_1}$$

$$\Rightarrow KE_2 = (0.99)^2 KE_1 \approx 1.02 KE_1$$

$$\% \text{ change in KE} = \frac{KE_2 - KE_1}{KE_1} \times 100 \approx 2\%$$

ILLUSTRATION 4.98

I. In which of the following situations, the heavier of the two particles has smaller de Broglie wavelength? The two particles

- Move with the same speed
- Move with the same linear momentum
- Move with the same kinetic energy
- Have fallen through the same height

II. The ratio of the de Broglie wavelength of a proton and α -particles will be 1 : 2 if their

- velocity are in the ratio 1 : 8
- velocity are in the ratio 8 : 1
- kinetic energy are in the ratio 1 : 64
- kinetic energy are in the ratio 1 : 256

III. If uncertainty in the measurement of position and momentum of an electron are equal then uncertainty in the measurement of its velocity is approximately:

- $8 \times 10^{12} \text{ m s}^{-1}$
- $6 \times 10^{12} \text{ m s}^{-1}$
- $4 \times 10^{12} \text{ m s}^{-1}$
- $2 \times 10^{12} \text{ m s}^{-1}$

Sol.

I. c.

$$\text{II. b. } \lambda = \frac{h}{mv}, \frac{\lambda_p}{\lambda_\alpha} = \frac{1}{2} \Rightarrow \frac{(mv)_p}{(mv)_\alpha} = \frac{2}{1}$$

$$\therefore m_\alpha = 4m_p \Rightarrow \frac{V_p}{V_\alpha} = \frac{8}{1}$$

$$\frac{KE_p}{KE_\alpha} = \frac{1/2 m_p V_p^2}{1/2 m_\alpha V_\alpha^2} = \frac{8^2}{4} = 16:1$$

III. a. Heisenberg's uncertainty principle is

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad \text{Given } \Delta x = \Delta p = m\Delta v$$

$$\Rightarrow \Delta p \geq \sqrt{\frac{h}{4\pi}} \text{ i.e. } m\Delta v \geq \sqrt{\frac{h}{4\pi}}$$

$$\Rightarrow \Delta v \geq \frac{1}{m} \sqrt{\frac{h}{4\pi}} \geq 8 \times 10^{12} \text{ m s}^{-1}$$

CONCEPT APPLICATION EXERCISE 4.1

Objective Type

- The ratio of the energies of photons of wavelengths 2000 Å and 4000 Å is
(1) 2 (2) 4 (3) 1/2 (4) 1/4
- Bohr's atomic model can explain
(1) The spectrum of hydrogen atom only
(2) The spectrum of an atom or ion containing one electron only
(3) The spectrum of hydrogen molecule
(4) The solar spectrum.
- The wavenumber of the first Balmer line of Li^{2+} ion is 136800 cm^{-1} . The wavenumber of the first line of Balmer series of hydrogen atom is (in cm^{-1})
(1) 68400 (2) 15200 (3) 76000 (4) 30800
- If the uncertainty in the position of an electron is zero, the uncertainty in its momentum will be
(1) $< \frac{h}{4\pi}$ (2) $> \frac{h}{4\pi}$ (3) Zero (4) Infinity
- If the following matter waves travel with equal velocity, the longest wavelength is that of a/an
(1) Electron (2) Proton
(3) Neutron (4) α -Particle
- Which of the following postulates does not belong to Bohr's model of atom?
(1) Angular momentum is an integral multiple of $h/2\pi$.
(2) The electron stationed in the orbit is stable.
(3) The path of an electron is circular.
(4) The change in the energy levels of electron is continuous.

ANSWERS

Objective Type

- (1)
- (2)
- (2)
- (4)
- (1)
- (4)

4.29 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, which is based on Newton's law of motion, successfully describes the motion of all macroscopic objects such as moving car, falling stone, orbiting planets, etc. These objects have essentially a particle-like behaviour. However, it failed when applied to microscopic objects such as electrons, atoms, molecules, etc. This is because these microscopic properties have both observable wave-like and particle-like properties and classical mechanics ignores the concept of dual behaviour of matter, especially for subatomic particles, and the uncertainty principle. In order to explain the behaviour of electrons and other microscopic particles, a new branch of science called **quantum mechanics** was developed.

Quantum mechanics is a theoretical science that deals with the study of the motions of microscopic objects that have both

observable wave-like and particle-like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave-like properties are insignificant), the result are same as those from classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Erwin Schrödinger described the behaviour of electrons around the nucleus by a mathematical equation known Schrödinger wave equation.

The Schrödinger wave equation for the wave motion of an electron in an atom moving in three-dimensional space is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

where x , y , and z are space coordinates, m is the mass of the electron, h is Planck's constant, E is the total energy, and V is the potential energy of the electron, ψ (Greek letter psi) is the amplitude of the wave, called the wave function and $\partial^2 \psi / \partial x^2$ refers to the second derivative of ψ with respect to x only and so on.

Sometimes the Schrödinger wave equation is written in the form

$$\hat{H}\psi = E\psi,$$

where \hat{H} is the total energy operator called the Hamiltonian operator. The Hamiltonian operator is the sum of kinetic energy operator (\hat{T}) and potential energy operator (\hat{V}) i.e.,

$$\hat{H} = \hat{T} + \hat{V}$$

Substituting the value of \hat{H} in the above equation, we get

$$(\hat{T} + \hat{V})\psi = E\psi$$

This equation is solved to get the value of E and ψ for the system. Thus, the quantum mechanical study of any system involves the following:

- Write the Schrödinger wave equation for the system.
- Solve the Schrödinger wave equation to get acceptable solutions to wave functions and their corresponding energies.
- The wave function contains within it all possible information that can be known about a system.
- The observable properties of the system are then calculated from ψ .

Acceptable solutions to the wave equation, that is physically possible solutions, must have certain properties:

- ψ must be continuous.
- ψ must be finite.
- ψ must be single valued.
- The probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one.

The probability of finding an electron at a point (x, y, z) is ψ^2 . So,

$$\int_{-\infty}^{+\infty} \psi^2 dx dy dz = 1$$

Several wave functions called $\psi_1, \psi_2, \psi_3, \dots$, will satisfy these conditions to the wave equation and each of these has a corresponding energy E_1, E_2, E_3, \dots . Each of these wave functions

ψ_1, ψ_2 , etc., is called an *orbital*, by analogy with the *orbits* in Bohr theory. In the hydrogen atom, the single electron occupies the lowest energy level E_1 , called ground state. The corresponding wave function ψ_1 describes the orbital, that is the volume in space where there is a high probability of finding the electron.

There are a number of acceptable solutions to the wave equation and each orbital is described by three quantum numbers; n, l , and m .

4.30 HYDROGEN ATOM AND THE SCHRÖDINGER EQUATION

Quantum mechanical treatment of the hydrogen atom: A hydrogen atom is the simplest chemical system consisting of one proton and one electron. Assuming that the electron moves at a distance r around the stationary nucleus, the nucleus can be taken as the origin of a coordinate system. The Schrödinger equation for the hydrogen atom can be written in terms of the Cartesian coordinates (x, y, z) or in terms of the spherical polar coordinates (r, θ, ϕ) of the electron with respect to the nucleus. Since an atom has spherical symmetry, it is more convenient to write Schrödinger equation in terms of polar coordinates. The relationships between the two coordinate systems are shown in Fig. 4.26.

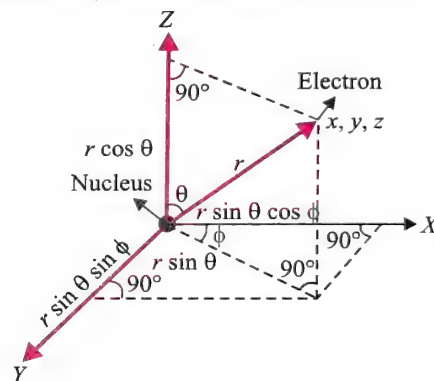


Fig. 4.26 Relationship between Cartesian (x, y, z) and polar coordinates (r, θ, ϕ)

The coordinates x, y and z of the electron with respect to nucleus in terms of polar coordinates are given by:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$x^2 + y^2 + z^2 = r^2$$

When the Schrödinger equation in polar coordinates is solved for the hydrogen atom, it gives the possible energy states and the corresponding wave function $[\psi(r, \theta, \phi)]$ (called *atomic orbitals* or *hydrogenic orbitals*, which are in fact the mathematical function of the coordinates of the electron associated with each energy state). It can be shown that an atomic orbital is the product of two factors: (i) the radial part, dependent on r and (ii) the angular part, dependent on θ and ϕ . The quantized electronic states of the hydrogen atom are given by

$$E_n = \frac{-m_e e^4}{8\epsilon_0^2 h^2 n^2} \text{ (in SI units)}$$

where m_e is the mass of electron in kilogram, e is its charge in coulomb, h is the Planck's constant, and n is the principal quantum

number. It is interesting to note that the electronic energy of the hydrogen atom depends only on n and is independent of l and m .

The above quantised energy states and corresponding wave functions, which are characterised by a set of three quantum numbers (principal quantum number n , azimuthal quantum number l , and magnetic quantum number m_l), arise as a natural consequence in the solution to the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical solution to the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum and other phenomena that could not be explained by the Bohr model.

The quantum mechanical approach has gained wide acceptance as the results obtained are in excellent agreement with experimental findings. In particular, the Schrödinger equation is very well suited to interpret the experimental information about the structures of atoms and molecules.

The Schrödinger equation cannot be exactly solved for a multi-electron atom. However, solutions with reasonable accuracy can be obtained using approximate methods. The total wave function of a multi-electron atom can be constructed from atomic orbitals having different energies. These atomic orbitals are the functions of coordinates of a single electron and their angular part has the same form as that for the hydrogen atom depending upon l and m_l values. However, their radial part is different and also takes into account the mutual repulsion between the electrons and depends on n , l , and charge Z on the nucleus. According to the quantum mechanical model of atom, these *atomic orbitals* form the basis of the electronic structure of atoms. In a multi-electron atom, the electrons are filled in various orbitals in order of increasing energy.

4.30.1 IMPORTANT FEATURES OF THE QUANTUM MECHANICAL MODEL OF ATOMS

The quantum mechanical model of atom is the picture of the structure of the atom, which results from the application of the Schrödinger equation to the atom. The important features of the quantum mechanical model are listed below:

- The energy of an electron in an atom is quantised, i.e., the electron can have only certain specific values.
- The existence of quantised electronic energy states is a direct consequence of the wave properties of electrons and are acceptable solutions to the Schrödinger wave equation.
- The exact position and velocity of an electron in an atom cannot be determined simultaneously. Therefore, it is not possible to determine the exact trajectory of the electron. Hence, we consider the probability of finding the electron at different positions in the atom.
- The wave function ψ for an electron represent an atomic orbital in an atom. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons.
- The wave function ψ is the storehouse of all information about an electron in an atom, and by quantum mechanics one can extract this information out of ψ .

- The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function $(\psi)^2$ at that point. $(\psi)^2$ is known as the **probability density** and is always positive.

Significance of wave function: Mathematically, ψ is a function of the wave equation with which the equation can be solved. Physically, ψ represents the amplitude of an electron wave at any time. Just as in case of light wave, the intensity of light is proportional to the square of the amplitude of wave, similarly in case of electron wave, the square of the wave function (ψ^2) represents the intensity of an electron at that point. In other words, ψ^2 determines the probability of finding the electron per unit volume in a given region of the space around the nucleus. Therefore, as we consider the electron in terms of the probability of it being present in a space, ψ^2 is called probability density and ψ is called probability amplitude. The Schrödinger wave equation is a second order differential equation. Thus we may obtain any values of ψ . But all the values of ψ may not be significant. The significant values of ψ are called eigen functions, and the corresponding energy values are called eigenvalues.

4.31 CONCEPT OF ORBITALS

Bohr's concept of well-defined **orbits** along which electrons revolve around the nucleus in an atom is ruled out with the consequence of Heisenberg uncertainty principle. According to this) it is not possible to determine precisely the position and momentum of an electron in an atom. In the quantum mechanical model, we talk about certain regions in the space around the nucleus where the probability of finding the nucleus is maximum. Such regions are expressed by mathematical expressions and are called orbital wave functions or commonly known as orbitals. Therefore, the wave equation leads to the concept of orbitals instead of well-defined circular orbits.

An orbital may be defined as a region in the space around the nucleus where the probability of finding the electron is maximum.

The probability of finding the electron does not become zero even at a large distance from the nucleus, although it may become negligible. Therefore, it is impossible to draw a boundary that will enclose the region of 100% probability of finding the electron. However, for the sake of simplicity, we draw arbitrary boundaries that enclose the regions where the probability of finding the electron is maximum (about 90–95%).

The electron density method is used to represent an orbital (Fig. 4.27). The intensity of dots represents the probability of finding an electron in a particular region.

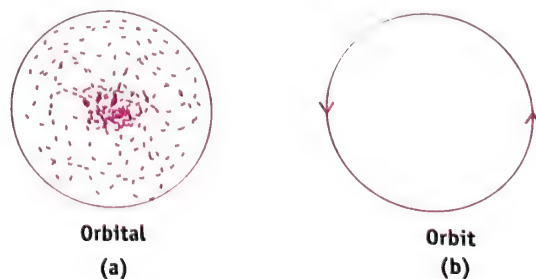


Fig. 4.27 Representation of (a) electron density of an orbital and (b) Bohr orbit

In an atom, there are a large number of orbitals. These orbitals are quantitatively distinguished from each other by their shape, size, and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly, shape and orientation mean that there is more probability of finding the electron along certain directions than others.

The important differences between an orbit and an orbital are listed in Table 4.9.

Table 4.9 Differences between orbit and orbital

Orbit	Orbital
1. An orbit refers to the circular path in which an electron revolves around the nucleus.	1. An orbital refers to the region of space having the maximum probability of finding an electron around the nucleus.
2. An orbit represents the motion of an electron around the nucleus in a plane.	2. An orbital represents the motion of an electron around nucleus in three-dimensional space.
3. An orbit (n) can accommodate a maximum of $2n^2$ electrons.	3. An orbital can accommodate a maximum of two electrons.
4. Orbits are designated as K, L, M, etc., or 1, 2, 3 etc., from the nucleus outwards.	4. Orbitals are designated as d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2} , p_x , p_y , p_z etc.
5. Orbits are circular in shape.	5. Orbitals have different shapes, e.g., s orbitals are spherically symmetrical whereas p orbitals are dumb-bell shaped.

4.32 QUANTUM NUMBERS

A large number of orbitals are possible in an atom. These orbitals are designated by a set of number known as quantum numbers. In order to specify size, energy, shape, and orientation of orbitals, three quantum numbers are required. These are principal quantum number (n), azimuthal quantum number (l), and magnetic quantum number (m_l). In order to specify the electron, an additional quantum number, called the spin quantum number (S), is needed. Thus, each orbital in an atom is designated by a set of three quantum numbers while each electron is designated by a set of four quantum numbers.

- a. Principal quantum number (n):** This is the most important quantum number as it determines the size and to large extent the energy of the orbital. For hydrogen and hydrogen-like species (He^{\oplus} , Li^{2+} , ...), energy and size of the orbital depend only on n . The average energy of the electron is directly proportional to the principal quantum number, i.e., $E \propto n$. As the energy is required in moving away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with an increase in n . The size of an orbital increases with an increase in the principal quantum number ($\text{size} \propto n$). In other words, for higher values of n , the electron will be located away from the nucleus. The principal quantum number can assume any positive integral value of n (1, 2, 3...). It also identifies the *energy level* or *energy shell*, designated as K, L, M, N, ..., etc., corresponding to the number of n .

The maximum number of electrons in a shell is given by $2n^2$.

For example

n	1	2	3	4	...
Shells	K	L	M	N	...
Maximum number of electrons ($2n^2$)	2	8	18	32	...

- b. Azimuthal quantum number (l):** It is also known as orbital angular momentum or subsidiary quantum number. This quantum number determines the angular momentum of the electron and defines the three-dimensional shape of the orbital. The value of l gives the sub-level or sub-shell in which the electron is located. The number of sub-shells within a principal shell is determined by the value of n for that principal energy level. For a given value of n , l can have values ranging from 0 to $n - 1$. The number of sub-shells (l) in a principal shell is equal to the value of n . For example, in the first shell ($n = 1$), there is only one sub-shell, which corresponds to $l = 0$. For the second shell ($n = 2$), there are two sub-shells ($l = 0, 1$) and three ($l = 0, 1, 2$) in the third shell ($n = 3$), and so on. Each sub-level or sub-shell is assigned an azimuthal quantum number (l). They are represented by following symbols:

Value of l	0	1	2	3	4	5	...
Designation of sub-shell	s	p	d	f	g	h	...

The names s , p , d , and f are derived from spectroscopic terms sharp, principal, diffuse, and fundamental, respectively.

The relation between the orbital angular momentum and azimuthal quantum number (l) is

Orbital angular momentum

$$= \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \hbar \quad \left(\hbar = \frac{h}{2\pi} \right)$$

Table 4.10 shows the permissible values of l for a given principal quantum number and the corresponding sub-shell notation.

Table 4.10. Sub-shell notations

n	l	Subshell notation
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

- c. Magnetic quantum number (m_l):** The magnetic quantum number denoted by m_l gives information about the spatial orientation of orbitals with respect to a standard set of coordinate axes. These different orientations are called orbitals. The number of orbitals in a particular sub-shell within a principal energy level is given by permitted values

of m_l which in turn depend on the values of l . The possible values of m_l range from $+l$ through 0 to $-l$, thus making a total of $2l + 1$ values, i.e.,

$$m_l = -l, -(l-1), -(l-2) \dots 0, 1, \dots, (l-2), (l-1), l.$$

For $l = 0$ (i.e., s sub-shell), $m_l = 0$, $[2(0) + 1] = 1$. It means that s sub-shell has only one orbital.

For $l = 1$ (i.e., p sub-shell), $m_l = -1, 0, +1$, $[2(1) + 1] = 3$. It means p sub-shell has three orbitals.

For $l = 2$ (i.e., d sub-shell), $m_l = -2, -1, 0, +1, +2$, $[2(2) + 1] = 5$. It means d sub-shell has five orbitals.

The relation between sub-shells and the number of orbitals associated with them given below:

Table 4.11 Relation between sub-shell and orbital

Value of l	0	1	2	3	4	5
Sub-shell notation	s	p	d	f	g	h
number $(2l + 1)$ of orbitals	1	3	5	7	9	11

- d. **Spin quantum number (m_s):** In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number and depicted it as the electron spin quantum number (m_s). This quantum number does not follow from the wave mechanical treatment but arises from the spectral evidence. In the line spectra of multi-electron atoms, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines closely spaced), etc. All the three above-mentioned quantum numbers are not enough to explain the observations that can be explained by the spin quantum number.

An electron in its motion around the nucleus also rotates or spins about its own axis as the earth spins around its own axis while revolving around the sun. Hence, the electron has, besides charge and mass, an intrinsic spin angular quantum number.

The spin angular momentum is depicted by the symbol μ_s . The values of μ_s can be found out from the following expression:

$$\mu_s = \sqrt{s(s+1)} \frac{h}{2\pi}$$

The spin angular momentum of the electron—a vector quantity—can have two orientations relative to the chosen axis. These two orientations have the values $+1/2$ or $-1/2$. These are called the spin states of the electron and are represented by two arrows: \uparrow (spin up) and \downarrow (spin down) (Fig. 4.28). Two electrons that have different m_s values (one $+1/2$ and other $-1/2$) are said to have opposite spins. An orbitals cannot hold more than two electrons, and these two electrons should have opposite spins.

The spin of electrons is responsible for most of the magnetic properties of atoms, molecules, or ions. Due to their spin, electrons behave as tiny magnets. If all the electrons in an atom or molecule are paired, they behave as a diamagnetic substance, i.e., it is weakly repelled by the magnetic field. On the other hand, if atoms or molecules of a substance have one or more unpaired electrons, it behaves as a paramagnetic substance i.e., it is weakly attracted by the magnetic field. The magnetic moment of a paramagnetic substance is related to the number of unpaired electrons in the species as

$$\text{Magnetic moment} = \sqrt{n(n+2)} \cdot \mu_B$$

where μ_B = Bohr magneton, a unit of magnetic moment

n = Number of unpaired electrons

The above magnetic moment is spin only magnetic moment.

Note: The spin quantum number can have only two values, namely, $+1/2$ and $-1/2$, which differ from each other by unity as the values of other quantum numbers do.

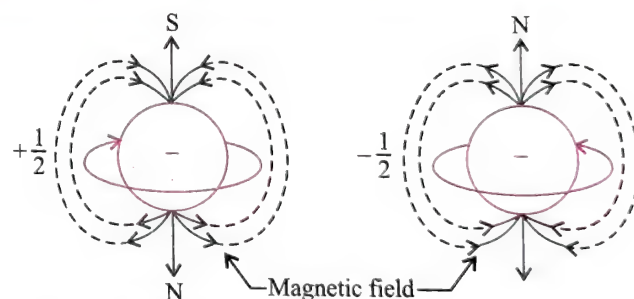


Fig. 4.28 Spinning of an electron about its own axis in clockwise and anti-clockwise directions. Clockwise and anti-clockwise spinings of the electron produce magnetic fields

Table 4.12 Quantum numbers and their significance

Quantum number	Symbol	Restrictions	Range of values	Significance
Principal quantum number	n	Positive integers	1, 2, 3, ...	Identifies shell, determines size and energy of orbital, number of orbitals in the n th shell = n^2
Azimuthal quantum number or Angular momentum quantum number or subsidiary or secondary quantum number	l	Positive integers less than n	0, 1, 2, $(n-1)$ Total possible values = n	Identifies sub-shell; determines shape of the orbital, energy of orbital in a multi-electron atom along with n and orbital angular momentum, i.e., $\sqrt{l(l+1)}h/2\pi$
Magnetic quantum number	m_l	Integers between $-l$ and $+l$	$-l$ to $+l$, including 0 Total possible values = $(2l+1)$	Determines orientation of the orbital
Magnetic spin quantum number	m_s	Half integers $+\frac{1}{2}$ or $-\frac{1}{2}$	$+\frac{1}{2}$ or $-\frac{1}{2}$	Determines orientation of the spin

ILLUSTRATION 4.99

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Sol. For $n = 3$, the possible values of l are 0, 1 and 2. Thus there is one $3s$ orbital ($n = 3, l = 0$ and $m_l = 0$); there are three $3p$ orbitals ($n = 3, l = 1$ and $m_l = -1, 0, +1$); there are five $3d$ orbitals ($n = 3, l = 2$, and $m_l = -2, -1, 0, +1, +2$).

Therefore total number of orbitals = $1 + 3 + 5 = 9$

The same value can be obtained by using the relation; number of orbitals = n^2 i.e., $3^2 = 9$

ILLUSTRATION 4.100

Using s, p, d, f notations, describe the orbital with the following quantum numbers.

- a. $n = 2, l = 1$ b. $n = 4, l = 0$
c. $n = 5, l = 3$ d. $n = 3, l = 2$

Sol.

n	l	orbital
a. 2	1	$2p$
b. 4	0	$4s$
c. 5	3	$5f$
d. 3	2	$3d$

ILLUSTRATION 4.101

The principal quantum number n of an atomic orbital is 5. What are the possible values of l ?

Sol. For the principal quantum number 5, the possible values of l are 0, 1, 2, 3, and 4.

ILLUSTRATION 4.102

Give the notation for the sub-shell denoted by the following quantum numbers:

- a. $n = 5, l = 2$ b. $n = 6, l = 3$
c. $n = 4, l = 0$ d. $n = 5, l = 4$

Sol. a. $5d$ b. $6f$ c. $4s$ d. $5g$

ILLUSTRATION 4.103

How many sub-shells are there in N shell? How many orbitals are there in d sub-shell?

Sol. For N shell, principal quantum number is $n = 4$.

Number of sub-shells in an energy level = n

\therefore Number of sub-shells in N shell = 4

For d subshell, $l = 2$.

Number of orbitals in a sub-shell = $2l + 1$

Number of orbitals in a d sub-shell = $2 \times 2 + 1 = 5$

ILLUSTRATION 4.104

Give the sets of quantum numbers that describe an electron in a $3p$ orbital.

Sol. In a $3p$ orbital, the principal quantum number (n) is 3, the azimuthal quantum number (l) is 1, the magnetic momenta are $m_l = +1, 0, -1$, the spin quantum number (m_s) is $+1/2$ or $-1/2$.

ILLUSTRATION 4.105

What is the maximum number of electrons that can be accommodated

- a. In the sub-shell with $l = 3$?
b. In the shell with $n = 3$?
c. In an orbital with $m_l = +3$?

Sol.

- a. For a sub-shell $l = 3$, number of orbitals = $2l + 1 = 2 \times 3 + 1 = 7$
 \therefore Number of electrons $2 \times 7 = 14$
b. For a shell with $n = 3$, the number of orbitals is $n^2 = 3^2 = 9$
 \therefore Number of electrons = $9 \times 2 = 18$
c. Orbital with $m_l = +3$ corresponds to only one orbital and hence it can accommodate only two electrons.

ILLUSTRATION 4.106

Which of the following orbitals are not possible?

$2d, 4f, 4g$, and $6d$

Sol. **$2d$ is not possible:** for d sub-shell $l = 2$, when $n = 2$, l can be equal to 0 and 1. Hence, l cannot be 2 for $n = 2$ so that $2d$ sub-shell is not possible.

$4f$ is possible: for f sub-shell $l = 3$, when $n = 4$, l can be equal to 3.

$4g$ is not possible: for g sub-shell $l = 4$, when $n = 4$, l cannot be equal to 4.

$6d$ is possible: for d sub-shell $l = 2$, when $n = 6$, l can be equal to 2.

ILLUSTRATION 4.107

What is the lowest value of n that allows g orbitals to exist?

Sol. For g sub-shell, $l = 4$. The minimum value of n for which l can be 4 is $4 + 1$ or 5.

ILLUSTRATION 4.108

How many orbitals are possible in

- a. 4th energy level b. $5f$ sub-shell

Sol.

- a. In the fourth energy level, the value for the principal quantum number is 4.
 \therefore Number of orbitals in $n = 4$ is $n^2 = 4^2 = 16$
b. In $5f$ sub-shell, $l = 3$.
 \therefore Number of orbitals = $(2l + 1) = 2 \times 3 + 1 = 7$

ILLUSTRATION 4.109

The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{l(l+1)} \frac{h}{2\pi}$. What is the momentum of an s-electron?

Sol. For s electron, l has a value of 0.

Thus the momentum of s electron is $\sqrt{0(0+1)} \frac{h}{2\pi} = 0$

ILLUSTRATION 4.110

What is the difference in the angular momentum associated with the electron in two successive orbits of a hydrogen atom?

Sol. The angular momentum of an electron in an orbit is an integral multiple of $h/2\pi$. Therefore, the difference in the angular momentum associated with the electron in two successive orbits of hydrogen atom is $h/2\pi$.

ILLUSTRATION 4.111

What should be the value of the spin quantum number of the last electron in d^9 configuration?

Sol. The value of spin quantum number (s) can be $+1/2$ or $-1/2$ because an electron can rotate on its axis either in clockwise or in anti-clockwise direction. But one quantum number depicts one electron and thus its value will be $-1/2$ for d^9 configuration.

ILLUSTRATION 4.112

What is the orbital angular momentum of a d electron?

Sol. Orbital angular momentum = $\sqrt{l(l+1)} \frac{h}{2\pi}$

For d electron, $l = 2$.

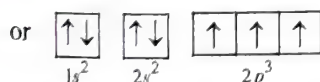
\therefore Orbital, angular momentum

$$= \sqrt{2(2+1)} \frac{h}{2\pi} = \sqrt{6} \frac{h}{2\pi}$$

ILLUSTRATION 4.113

What is the total spin and magnetic moment of an atom with atomic number 7?

Sol. The atomic number of the element is 7. So the electronic configuration is $1s^2 2s^2 2p^3$



Therefore, the number of unpaired electron is (n) 3.

$$\text{Total spin of electrons} = \pm \frac{1}{2}n = \pm \frac{1}{2} \times 3 = \pm \frac{3}{2}$$

$$\text{Magnetic moment of the element} = \sqrt{n(n+2)}\text{BM}$$

$$= \sqrt{3(3+2)}\text{BM}$$

$$= \sqrt{15}\text{BM}$$

ILLUSTRATION 4.114

I. What is the total numbers of orbitals and electrons for $m = 0$, if there are 30 protons in an atom?

- 7 orbitals, 14 electrons
- 6 orbitals, 12 electrons
- 5 orbitals, 10 electrons
- 3 orbitals, 6 electrons

II. The quantum numbers $+1/2$ and $-1/2$ for the electron spin represent

- Rotation of the electron in clockwise and anti-clockwise directions, respectively
- Rotation of the electron in anti-clockwise and clockwise directions, respectively
- Magnetic moment of the electron pointing up and down, respectively
- Two quantum mechanical spin states which have no classical analogue

III. Which of the following statements is correct?

- $(n-1)d$ sub-shell has lower energy than ns sub-shell
- $(n-1)d$ sub-shell has higher energy than ns sub-shell
- $(n+1)d$ sub-shell has lower energy than nf sub-shell
- nf sub-shell has lower energy than $(n+2)s$ sub-shell

IV. The radial probability is the probability of finding electrons in a small spherical shell around the nucleus at a particular distance (r). Hence, radial probability is

- $4\pi r^2 dr \psi^2$
- $(4/3) \pi r^2 dr \psi^2$
- $2\pi r^2 dr \psi^2$
- $4\pi r dr \psi$

Sol.

I. a. The configuration of the atom of atomic number 30 is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$. This will have 7 orbitals of $m = 0$. In 7 orbitals number of electrons are $7 \times 2 = 14$.

II. d.

III. b.

IV. (a) $R = 4\pi r^2 dr \psi^2$

ILLUSTRATION 4.115

I. The z-component of angular momentum of an electron in an atomic orbital is governed by the

- Principal quantum number
- Azimuthal quantum number
- Magnetic quantum number
- Spin quantum number

II. Which of the following sets of quantum numbers represents an impossible arrangement?

	n	l	m_l	m_s
a.	3	3	-2	1/2
b.	4	0	0	1/2
c.	3	2	-2	1/2
d.	5	3	0	1/2

III. The principal quantum number of an atom is related to the

- Size of the orbital
- Spin angular momentum
- Orbital angular momentum
- Orientation of the orbital in space

IV. Which of the following should be the possible sub-shells for $n + l = 7$?

- $7s\ 6p\ 5d\ 4f$
- $4f\ 5p\ 6s\ 4d$
- $7s\ 6p\ 5d\ 6d$
- $4s\ 5d\ 6p\ 7s$

Sol.

I. c. Magnetic quantum number (m).

II. a. l cannot be equal to n .

III. (a)

- IV. a. $n + l = 7$
 $7 + 0 = 7s$
 $6 + 1 = 6p$
 $5 + 2 = 5d$
 $4 + 3 = 4f$

ILLUSTRATION 4.116

I. What is the maximum number of electrons in the possible sub-shells for $n + l = 4$?

- 8
- 6
- 12
- 16

II. The sub-shell $2d$ is not possible because

- $n \neq l$
- $l > n$
- $n < l$
- None of these

III. What is the maximum number of elements if the elements above $n = 4$ do not exist in nature?

- 40
- 60
- 44
- 108

IV. Give the values of all the four quantum numbers for $2p$ electrons in nitrogen ($Z = 7$).

Sol.

- I. a. $n + l = 4$ Maximum number of electrons
 $4 + 0 = 4s = 2$
 $3 + 1 = 3p = 6$
Total = 8

II. a. For sub-shell $2d$, $n = 2$ and $l = 2$, and the values of n and l can never be equal.

III. b. Since, $n = 1, 2, 3$, and 4 ,

$$\frac{1s}{2}, \frac{2s\ 2p}{8}, \frac{3s\ 3p\ 3d}{18}, \frac{4s\ 4p\ 4d\ 4f}{32}$$

Thus, total number of existent elements is $2 + 8 + 18 + 32 = 60$.

IV. The electronic configuration of nitrogen atom is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

For the $2p$ electrons, $n = 2$, $l = 1$, $m = -1, 0, +1$, $s = +1/2$ or $-1/2$

(All $2p$ electrons have parallel spins.)

ILLUSTRATION 4.117

I. Arrange the electrons represented by the following sets of quantum numbers in decreasing order of energy.

- $n = 4, l = 0, m = 0, s = +1/2$
- $n = 3, l = 1, m = 1, s = -1/2$
- $n = 3, l = 2, m = 0, s = +1/2$
- $n = 3, l = 0, m = 0, s = -1/2$

II. Which of the following sets of quantum numbers represents an impossible arrangement?

	n	l	m	s
a.	3	2	-2	1/2
b.	4	0	0	1/2
c.	3	2	-3	1/2
d.	5	3	0	1/2

III. Principal, azimuthal, and magnetic quantum numbers are, respectively, related to

- Size, orientation, and shape
- Size, shape, and orientation
- Shape, size, and orientation
- None of these

IV. Which of the following statements is/are wrong?

- If the value of $l = 0$, the electron distribution is spherical.
- The shape of the orbital is given by magnetic quantum number.
- The angular momentums of $1s$, $2s$, and $3s$ electrons are equal.
- In an atom, all electrons travel with the same velocity.

Sol.

- I. a. Represents $4s$ electron
b. Represents $3p$ electron
c. Represents $3d$ electron
d. Represents $3s$ electron

II. c. For $l = 2$, $m = -2, -1, 0, +1, +2$

III. b. Principal quantum number gives size, azimuthal gives shape, and magnetic gives orientation.

IV. (a, b) Option (b) is wrong because shape is given by azimuthal quantum number and magnetic quantum number tells the orientation. Option (d) is wrong because electrons in different shells travel with different velocities.

Hence, (a) and (c) are the correct answers.

ILLUSTRATION 4.118

- I. The sum of all the quantum numbers of hydrogen atom is
 a. 1 b. 0 c. $+\frac{1}{2}$ d. $\frac{3}{2}$
- II. The orbital angular momentum quantum number of the state s_2 is
 a. 0 b. $\sqrt{2} \frac{h}{2\pi}$ c. 1 d. $2 \cdot \frac{h}{2\pi}$
- III. In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields?
 I. $n = 1, l = 0, m = 0$ II. $n = 2, l = 0, m = 0$
 III. $n = 2, l = 1, m = 1$ IV. $n = 3, l = 2, m = 1$
 V. $n = 3, l = 2, m = 0$
 a. I and II b. II and III
 c. III and IV d. IV and V

Sol.

- I. d. The atomic number of H is 1

Quantum numbers are $n = 1, l = 0, m = 0, s = \frac{1}{2}$

$$\therefore \text{Total quantum number} = 1 + \frac{1}{2} = \frac{3}{2}$$

Hence, (d) is the correct choice.

- II. b. s_2 i.e., $3p: l = 1$

$$\begin{aligned} \text{Orbital angular momentum} &= \sqrt{l(l+1)} \cdot \frac{h}{2\pi} \\ &= \sqrt{1(1+1)} \cdot \frac{h}{2\pi} = \sqrt{2} \frac{h}{2\pi} \end{aligned}$$

- III. (b, d)

IV: $3d_{x^2-y^2}$; V: $3d_{z^2}$: Degenerate orbitals

II: $2s$; III: $2p$: (Assumed to have same energies in the absence of magnetic and electric fields)

ILLUSTRATION 4.119

What is the total number of pairs of electrons having at least three same quantum numbers of Be?

Sol. Be: ($Z = 4$)

Electronic configuration is $1s^2 2s^2$

For s electrons, the quantum number are

$$n = 1, l = 0, m = 0, s = \frac{1}{2} \quad \dots (i)$$

$$n = 1, l = 0, m = 0, s = -\frac{1}{2} \quad \dots (ii)$$

$$n = 2, l = 0, m = 0, s = \frac{1}{2} \quad \dots (iii)$$

$$n = 2, l = 0, m = 0, s = -\frac{1}{2} \quad \dots (iv)$$

Clearly, there are four possible groups: (i) and (ii), (iii) and (iv), (i) and (iii), and (ii) and (iv)

ILLUSTRATION 4.120

- I. The magnetic moment of M^{+} (atomic number = 25) is $\sqrt{15}$ BM. The number of unpaired electrons and the value of x , respectively, are

a. 4, 3 b. 3, 4 c. 3, 2 d. 5, 2

- II. Which of the following is(are) correct for H atom?

i. $1s < 2s < 2p < 3s < 3p$ ii. $1s < 2s = 2p < 3s = 3p$

iii. $1s < 2p < 3d < 4s$ iv. $1s < 2s < 4s < 3d$

The correct choice is

a. (ii), (iii) b. (i), (iv)

c. (i), (iii) d. (ii), (iv)

- III. The correct order of decreasing energies of the electrons is:

a. Electron 3 > Electron 4 > Electron 1 > Electron 2

b. Electron 4 > Electron 3 > Electron 1 > Electron 2

c. Electron 3 > Electron 4 > Electron 2 > Electron 1

d. Electron 3 > Electron 1 > Electron 4 > Electron 2

		n	l	m	s
1.	Electron 1	3	1	1	$\frac{1}{2}$
2.	Electron 2	3	0	0	$\frac{1}{2}$
3.	Electron 3	4	0	0	$-\frac{1}{2}$
4.	Electron 4	3	2	2	$\frac{1}{2}$

Sol.

- I. b. M^{+} ($Z = 25$): electronic configuration is

$1s^2 2s^2 2p^6 3d^5 4s^2 3s^2 3p^6$

or $d^5 = \uparrow \uparrow \uparrow \uparrow \uparrow$

Magnetic moment = $\sqrt{n(n+2)}$ BM

$$= \sqrt{5(5+2)} \text{ BM} = \sqrt{35} \text{ BM}$$

But given magnetic moment is $\sqrt{15} \text{ BM}$ or $\sqrt{3(3+2)} \text{ BM}$.

Hence, unpaired electrons = 3

Therefore, the oxidation number is 4.

- II. b. (i), (iv)

- III. b. Electron 4 > Electron 3 > Electron 1 > Electron 2

ILLUSTRATION 4.121

- I. The orbital having $m = -2$ should not be present in the following sub-shell:

a. d b. f c. g d. p

- II. What is the value of the spin quantum number of the last electron for d^9 configuration?

a. 0 b. $-\frac{1}{2}$ c. $\frac{1}{2}$ d. 1

III. All the energy levels are called excited states when the value of the principal quantum number is

- a. $n = 1$ b. $n > 1$ c. $n < 1$ d. $n > -1$

IV. If x is the number of electrons in an atom, the configuration should be expressed as

- a. l_x b. $n l^x$
c. nm^x d. None of these

Sol.

- I. d. For p sub-shell, $m = -1, 0, +1$. Therefore, $m = -2$ orbital will not be present in p sub-shell.
- II. b. The value of the spin quantum number (s) can be $+1/2$ or $-1/2$ because an electron can rotate along its axis either in clockwise or in anticlockwise direction. But one quantum number depicts one electron and thus its value will be $-1/2$ for d^9 configuration.
- III. b. All the energy states in which n is greater than 1 are called excited states.
- IV. b. The electronic configuration of an atom is expressed by first writing the principal quantum number (n), followed by the Azimuthal quantum number (l), and then writing the number of electrons (x) as superscript.

ILLUSTRATION 4.122

- I. What is the atomic number of an element if the quantum numbers of the highest energy electron of the element in the ground state are $n = 4$, $l = 1$, $m = -1$, $s = +1/2$?
- a. 31 b. 35 c. 30 d. 32
- II. The orbital $n = 6$, $l = 2$, and $m = 0$ will be designated as
- a. $6d_{z^2}$ b. $6d_{x^2-y^2}$
c. $6d_{xy}$ d. $6p_z$
- III. The orbital having $n = 2$, $l = 1$, and $m = 0$ is designated as
- a. $2p_z$ b. $2p_x$ c. $2p_y$ d. $3d_{z^2}$
- IV. How many electrons in a given atom can have the following quantum numbers
- a. $n = 4$, $l = 2$, $m = 0$
b. $n = 3$
c. $n = 2$, $l = 1$, $m = -1$, $s = +\frac{1}{2}$
d. $n = 4$, $l = 1$

Sol.

- I. a. The electronic configuration of the element will be $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1 4p^1$. Thus, the total number of electrons is 31, and hence the atomic number will be 31.
- II. a. For 6th of energy level $l = 2$ is for d sub-level, and $m = 0$, d_{z^2} orbital
- III. a. In the second or L energy level ($n = 2$), $l = 1$ for p orbital, $m = 0$ for z -axis. Hence, the orbital will be designated as $2p_z$.
- IV. a. $l = 2$ means d sub-shell and $m = 0$ refer to d_{z^2} orbital. Hence, the number of electrons is 2.

- b. For $n = 3$, $l = 0, 1, 2$

$l = 0$	$m = 0$	2 electrons
$l = 1$	$m = -1$	6 electrons
$l = 2$	$m = -2, -1, 0, +1, +2$	10 electrons
Total electrons		18 electrons

Alternatively, the number of electrons for any energy level is given by

$$2n^2 \quad \text{i.e., } 2 \times 3^2 = 18 \text{ electrons}$$

- c. $l = 1$ refers to p sub-shell, $m = -1$ refers to p_x or p_y orbital, whereas $s = +1/2$ indicates only one electron.
- d. $l = 1$ refers to p sub-shell which has three orbitals (p_x , p_y , and p_z) each having two electrons. Therefore, total number of electrons is 6.

ILLUSTRATION 4.123

- I. Which of the following set of quantum numbers is are not permitted?
- a. $n = 3$, $l = 2$, $m = -2$, $s = +\frac{1}{2}$
b. $n = 3$, $l = 2$, $m = -1$, $s = 0$
c. $n = 2$, $l = 2$, $m = +1$, $s = -\frac{1}{2}$
d. $n = 2$, $l = 2$, $m = +1$, $s = -\frac{1}{2}$
- II. The probability of finding the electron in p_x -orbitals is:
- a. maximum on two opposite side of the nucleus along x -axis
b. zero at the nucleus
c. same on all the sides around the nucleus
d. zero on the z -axis
- III. Which among the following electron will emit radiation of maximum wavelength?
- a. $n = 4$, $l = 1$, $m = 0$ to $n = 3$, $l = 2$, $m = -2$
b. $n = 3$, $l = 2$, $m = -2$ to $n = 3$, $l = 1$, $m = -1$
c. $n = 3$, $l = 2$, $m = 1$ to $n = 2$, $l = 0$, $m = 0$
d. $n = 3$, $l = 1$, $m = 0$ to $n = 2$, $l = 1$, $m = 1$
- IV. Which of the following has the maximum number of unpaired electrons?
- a. Mg^{2+} b. Ti^{3+} c. V^{3+} d. Fe^{2+}

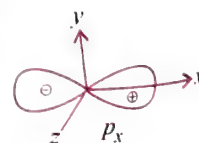
Sol.

- I. a. This set of quantum numbers is permitted.
b. This set of quantum numbers is not permitted as value of s cannot be zero.
c. This set of quantum numbers is not permitted as the value of l cannot be equal to n .
d. This set of quantum numbers is not permitted as the value of m cannot be greater than l .

- II. (a, b, d) For p_x : nodal plane contains z -axis

No electron can lie at nucleus

p_x gives space for probability of finding electron along x -axis and it will be maximum.



III. a. For $\lambda_{\max} E_{\text{radiated}} = \text{minimum} = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ i.e.

$\left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ has to be minimum.

This is independent of quantum numbers l , m and s .

Clearly, $n_1 = 3$ and $n_2 = 4$ minimize $E_{\text{radiation}}$.

IV. d. $\text{Fe}^{2+} = [\text{Ar}]3d^6 \Rightarrow 4$ unpaired e^-

Mg^{2+} has zero unpaired

V^{3+} has 2 unpaired and Ti^{3+} has 1 unpaired

4.33 ENERGIES OF ORBITALS AND ENERGY LEVEL DIAGRAM

4.33.1 ENERGY LEVEL DIAGRAM OF HYDROGEN ATOM

A diagram representing relative energies of various orbitals in an atom is called energy level diagram.

In hydrogen atom, the energy of an electron is determined solely by the principal quantum number (n). Thus, the energy of an electron increases with an increase in n . The energy of the orbitals increases as follows:

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$ so on and is depicted in Fig. 4.29.

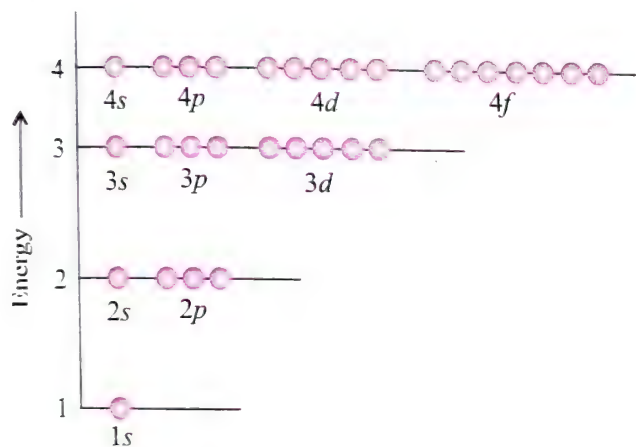


Fig. 4.29 Energy level diagram for hydrogen atom

In the energy level diagram, it may be noted that orbitals for the same value of principal quantum number (n) have the same energies even for different azimuthal quantum numbers (l). For example, the electron has the same energy when it is in $2s$ orbital as when it is present in $2p$ orbital although the shape of $2s$ and $2p$ orbitals are different. The orbitals having the same energy are called **degenerate orbitals**.

In hydrogen atom, there is only one electron present in $1s$ orbital; the orbital corresponds to the most stable condition and is called the **ground state**. In the ground state, the electron is most stable and is strongly held by the nucleus. However, in the *excited state*, the electron may present in any higher energy levels such as $2s$, $2p$, $3s$, and so on.

Thus, for an atom having a single electron, the principal quantum number (n) is only a parameter to determine the energy of the orbital. The value of l (azimuthal quantum number) merely determines the shape of the orbitals.

4.33.2 ENERGY LEVEL DIAGRAM OF MULTI-ELECTRON ATOMS

In case of multi-electron atoms, the energy of an electron, unlike that of a hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (sub-shell). As shown in Fig. 4.30, for a particular energy level or shell, the various sub-shells such as s , p , d , ... have different energies.

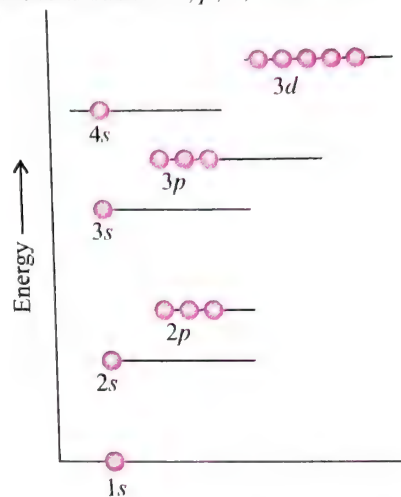


Fig. 4.30 Energy level diagram for multi-electron atoms

The main reason for having different energies of the sub-shells is the mutual repulsion among the electrons in a multi-electron atom. In hydrogen atom, there is only one electrical interaction present—the attraction between the negatively charged electron and the positively charged nucleus. But in a multi-electron atom, besides the attraction between the electron and the nucleus, there is repulsion between every electron and other electrons present in the atom. Thus, the stability of an electron in a multi-electron atom is due to the reason that the total attractive interactions are greater than the total repulsive interactions. The attractive interactions of an electron increase with an increase in positive charge (Z_e) on the nucleus. However, due to the presence of electrons in the inner shells, the electron in the outer shell does not experience the full positive charge of the nucleus (Z_e). It will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the **shielding** of the outer-shell electrons from the nucleus by the inner shell electrons, and the net positive charge experienced by the electron from the nucleus is known as **effective nuclear charge** (Z_{eff}).

i.e., $Z_{\text{eff}} = Z_e - \sigma$, where σ is the screening constant.

Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with an increase in nuclear charge.

The attractive and repulsive interactions of an electron depend upon the shell (n) and the shape (l) of the orbital in which the electron is present. For example, s orbitals being spherical in shape have maximum shielding effect as compared to p orbital. Similarly, p orbitals shield the electrons from the nucleus more than the d orbitals, even though all these orbitals are present in the same shell.

The shielding effect of various types of orbitals is in the order $s > p > d > f$ shielding or screening effect.

An electron in s orbital spends more time close to the nucleus in comparison to p orbital, and p orbital spends more time in the vicinity of the nucleus in comparison to d orbitals.

The order of attractive interaction in various types of orbitals is

$s > p > d > f$... attractive intersection

Electrons in various sub-shells experience different Z_{eff} . Z_{eff} experienced by the orbital decreases with an increase in the azimuthal quantum number (l). Thus, the s orbital will be more tightly bound to the nucleus than the p orbital and the p orbital in turn will be more tightly bound than the d orbital. The order of energies of various sub-shells within an energy level is

$$s < p < d < f \quad \dots \text{order of energies}$$

For a particular type of sub-shell, Z_{eff} decreases with an increase in the value of the principal quantum number n . Thus, $3d$ experiences lower Z_{eff} than $2s$.

$$4s < 3s < 2s < 1s \quad \dots \text{effective nuclear charge } (Z_{\text{eff}})$$

The energies of the orbitals in the same sub-shell decrease with an increase in the atomic number (Z_{eff}). For example, the energy of the $2s$ orbital of hydrogen atom is greater than that of the $2s$ orbital of a lithium atom, and that of lithium is greater than that of sodium and so on. That is,

$$E_{2s}(\text{H}) > E_{2s}(\text{Li}) > E_{2s}(\text{Na}) > E_{2s}(\text{K})$$

4.33.3 ($n + l$) OR BOHR-BURY RULE

As mentioned above, in a multi-electron atom, the energy of an electron depends upon the value of the principal quantum number (n) and the azimuthal quantum number (l). **The relative order of energies of various sub-shells in a multi-electron atom can be predicted with the help of the ($n + l$) rule or Bohr-Bury rule.**

- a. For an orbital, the lower the value of ($n + l$), the lower the energy.

For example, $4s$ orbital has lower energy than $3d$ orbital.

For $4s$ orbital, $n = 4$ and $l = 0$. Hence, $n + l = 4 + 0 = 4$

For $3d$ orbital, $n = 3$ and $l = 2$. Hence, $n + l = 3 + 2 = 5$

- b. If two orbitals have the same value of ($n + l$), the orbital with lower value of n will have the lower energy.

For example, consider $3p$ and $4s$ orbitals.

For $4s$ orbital, $n = 4$ and $l = 0$. Hence, $n + l = 4 + 0 = 4$

For $3p$ orbital, $n = 3$ and $l = 1$. Hence, $n + l = 3 + 1 = 4$

Here $3p$ orbital has lower energy than $4s$ because it has lower value of n .

Table 4.13 illustrates the ($n + l$) rule.

Table 4.13 Arrangement of orbitals with increasing energy on the basis of ($n + l$) rule

Orbital	Value on n	Value of l	Value of ($n + l$)	
1s	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	
2p	2	1	2 + 1 = 3	2p ($n = 2$) has lower energy than
3s	3	0	3 + 0 = 3	3s ($n = 3$)
3p	3	1	3 + 1 = 4	3p ($n = 3$) has lower energy than
4s	4	0	4 + 0 = 4	4s ($n = 4$)
3d	3	2	3 + 2 = 5	3d ($n = 3$) has lower energy than
4p	4	1	4 + 1 = 5	4p ($n = 4$)

ILLUSTRATION 4.124

The quantum numbers of electrons are given below: Arrange them in order of increasing energies.

- $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$
- $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
- $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$
- $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$
- $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$
- $n = 4, l = 1, m_l = +1, m_s = +\frac{1}{2}$

Sol. $e < b = d < c = f < a$

ILLUSTRATION 4.125

Among the following pairs of orbitals, which orbital will experience the largest effective nuclear charge?

- a. $2s$ and $3s$ b. $4d$ and $4f$ c. $3d$ and $3p$

Sol. a. $2s$, because $2s$ orbital lies nearer to the nucleus than $3s$ orbital.

b. $4d$, lies near to the nucleus.

c. $3p$, lies near to the nucleus.

ILLUSTRATION 4.126

The bromine atom possesses $3s$ electrons. It contains six electrons in $2p$ orbitals, six electrons in $3p$ orbitals and five electrons in $4p$ orbitals. Which of these electrons experience the lowest effective nuclear charge?

Sol. $4p$ electrons having the largest value of n are farthest from the nucleus, and hence experience the lowest effective nuclear charge. For orbitals of the same type of sub-shell, the greater the value of n the smaller the effective nuclear charge.

ILLUSTRATION 4.127

If the value of $n + l = 7$, then what should be the increasing order of energy of the possible sub-shells.

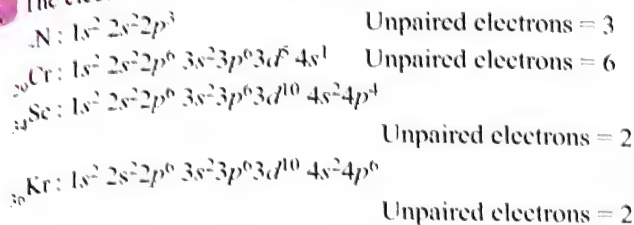
Sol. Given that $n + l = 7$
Hence $7 + 0 = 7s$
 $6 + 1 = 6p$
 $5 + 2 = 5d$
 $4 + 3 = 4f$

Thus the order of energy is $4f < 5d < 6p < 7s$.

ILLUSTRATION 4.128

Calculate the total spin and magnetic moment for atoms having atomic numbers 7, 24, 34, and 36.

Sol. The electronic configurations are as follows:



\therefore Total spin for an atom = $\pm \frac{1}{2} \times$ Number of unpaired electrons

For ${}_7\text{N}$, it is $\pm \frac{3}{2}$; For ${}_{24}\text{Cr}$, it is ± 3 .

For ${}_{34}\text{Se}$, it is ± 1 ; For ${}_{36}\text{Kr}$, it is 0.

Also magnetic moment = $\sqrt{n(n+2)}$

For ${}_7\text{N}$, it is $\sqrt{15}$; For ${}_{24}\text{Cr}$, it is $\sqrt{48}$.

For ${}_{34}\text{Se}$, it is $\sqrt{8}$; For ${}_{36}\text{Kr}$, it is $\sqrt{0}$.

4.34 RULES FOR FILLING OF ORBITALS IN AN ATOM

An atom in its ground state has the lowest energy, and it is most stable. The filling of orbitals in the ground state of atom takes place according to the aufbau principle, which is based on Pauli's exclusion principle, Hund's rule of maximum multiplicity, and the relative energies of the orbitals.

4.34.1 AUFBAU PRINCIPLE

The word 'aufbau' in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states that electrons are added progressively to the various orbitals in the order of increasing energies. The electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

The increasing order of energies of various orbitals is
 $1s 2s 2p 3s 3p 4s 3d 4p$
 $5s 4d 5p 4f 5d 6p 7s \dots$

The orbitals must be filled according to the above order.

Figure 4.31 illustrates a simple memory aid for remembering the increasing order of energies of various orbitals.

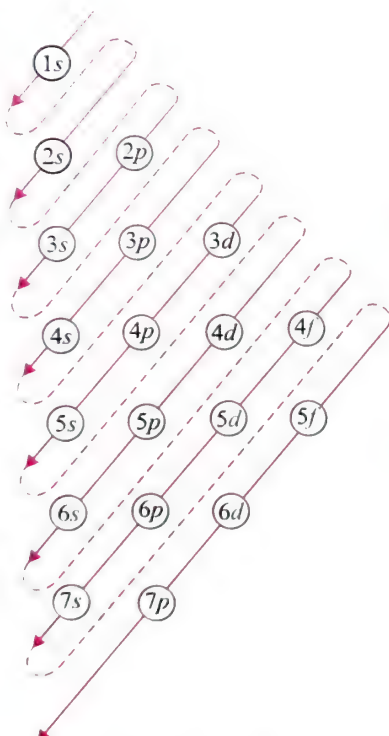


Fig 4.31 Order of filling of orbitals

4.34.2 PAULI EXCLUSION PRINCIPLE

Austrian scientist Wolfgang Pauli in 1926 put a restriction on filling electrons in various orbitals by his exclusion principle. This principle states that:

No two electrons in an atom can have the same set of four quantum numbers. The Pauli exclusion principle can also be stated as: Only two electrons may exist in the same orbital and these electrons must have opposite spin.

From this principle, it follows that the two electrons can have the same value of three quantum numbers n , l , and m_l , but must have opposite spin quantum number (i.e. either $+1/2$ or $-1/2$).

On the basis of this principle, it is possible to calculate the capacity of electrons to be present in any sub-shell. For example, sub-shell $1s$ comprises one orbital and thus the maximum number of electrons present in $1s$ sub-shell is two; in p and d sub-shells, the maximum number of electrons can be 6 and 10 and so on. Thus, it can be said: the maximum number of electrons in a shell with principle quantum number n is equal to $2n^2$.

4.34.3 HUND'S RULE OF MAXIMUM MULTIPLICITY

Hund's rule deals with the filling of electrons into the orbitals belonging to the same sub-shell. These orbitals have the same energy and are called degenerate orbitals. For example, $1p$ sub-shell has three orbitals and all the three orbitals have the same energy; hence they are degenerate.

This rule states that *the pairing of electrons in the orbital of a particular sub-shell (p , d , or f) does not take place until all the orbitals of the sub-shell are singly filled. Moreover, the singly occupied orbitals must have electrons with parallel spin.*

In p sub-shell, there are three, in d five, and in f seven orbitals; therefore, according to this rule, orbitals will be first filled with single electrons with parallel spin because this corresponds to minimum repulsion and the state of lower energy. The pairing of electrons will start in the p , d and f orbitals with the entry of fourth, sixth, and eighth electron.

ILLUSTRATION 4.129

The quantum numbers of the last electron of an element are given below. Predict the atomic number and name of the element from the following quantum numbers:

$$n = 3, l = 2, m = 0, s = -1/2$$

Sol. The given quantum numbers are as follows:

Principal quantum number (n) = 3

Azimuthal quantum number (l) = 2 or d

Magnetic quantum number (m) = 0

$$\begin{array}{|c|c|c|c|c|} \hline & & & & \\ \hline m = -2 & -1 & 0 & +1 & +2 \\ \hline \end{array}$$

d orbital

Spin quantum number (m_s) = $-\frac{1}{2}$

$$\text{or } \begin{array}{|c|c|c|c|c|} \hline \downarrow\uparrow & \downarrow\uparrow & \downarrow\uparrow & \uparrow & \uparrow \\ \hline -2 & -1 & 0 & +1 & +2 \\ \hline \end{array}$$

Therefore, total number of electrons in d orbital is 8. Hence, it is d^8 configuration, it shows that the element is Ni ($3d^8$).

Table 4.14 Distribution of electrons in various energy levels and their quantum numbers

Main energy level, n shell	Subsidiary energy level, l (sub-shell)	Sub-shell designation	Magnetic quantum number, m		Spin quantum number, s	Total electrons
1	0	1s	0		$+1/2, -1/2$	2 (Total = 2)
2	0	2s	0		$+1/2, -1/2$	2
	1	2p	-1	$2p_x$ or $2p_y$	$+1/2, -1/2$	6 (Total = 8)
			0	$2p_z$	$+1/2, -1/2$	
			+1	$2p_y$ or $2p_x$	$+1/2, -1/2$	
3	0	3s	0		$+1/2, -1/2$	2
	1	3p	-1	$3p_x$ or $3p_y$	$+1/2, -1/2$	6
			0	$3p_z$	$+1/2, -1/2$	
			+1	$3p_y$ or $3p_x$	$+1/2, -1/2$	
	2	3d	-2	$3d_{x^2-y^2}$ or $3d_{xy}$	$+1/2, -1/2$	10 (Total = 18)
			-1	$3d_{yz}$ or $3d_{zx}$	$+1/2, -1/2$	
			0	$3d_{z^2}$	$+1/2, -1/2$	
			+1	$3d_{zx}$ or $3d_{yz}$	$+1/2, -1/2$	
			+2	$3d_{xy}$ or $3d_{x^2-y^2}$	$+1/2, -1/2$	
4	0	4s	0		$+1/2, -1/2$	2
	1	4p	-1		$+1/2, -1/2$	6
			0		$+1/2, -1/2$	
			+1		$+1/2, -1/2$	
	2	4d	-2		$+1/2, -1/2$	10
			-1		$+1/2, -1/2$	
			0		$+1/2, -1/2$	
			+1		$+1/2, -1/2$	
			+2		$+1/2, -1/2$	
	3	4f	-3		$+1/2, -1/2$	14
			-2		$+1/2, -1/2$	
			-1		$+1/2, -1/2$	
			0		$+1/2, -1/2$	
			+1		$+1/2, -1/2$	
			+2		$+1/2, -1/2$	
			+3		$+1/2, -1/2$	
						Total = 32

ILLUSTRATION 4.130

Which combination of quantum numbers n , l , m and s for the electron in an atom does not provide a permissible solution to the wave equation?

a. $3, 2, -2, +\frac{1}{2}$

b. $3, 3, 1, -\frac{1}{2}$

c. $3, 2, 1, -\frac{1}{2}$

d. $3, 1, 1, -\frac{1}{2}$

Sol. b. $3, 3, 1, -1/2$ in the combination $n = 3, l = 3, m = 1, s = -1/2$ since l cannot have a value equal to n

ILLUSTRATION 4.131

Predict the atomic number and element from the following quantum numbers:

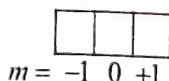
$$n = 2, l = 1, m = +1, s = -\frac{1}{2}$$

Sol. The given quantum number are as follows:

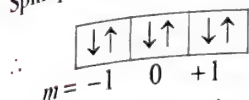
Principal quantum number (n) = 2

Azimuthal quantum number (l) = 1 or p orbital

Magnetic quantum number (m) = +1 or



Spin quantum number (m_s) = $-\frac{1}{2}$ or \downarrow



Hence, the configuration is $2p^6$.

Total electronic configuration is $1s^2 2s^2 2p^6$.

The element is Ni (atomic number = 10).

ILLUSTRATION 4.132

For each of the following pairs of hydrogen orbitals, indicate which is higher in energy.

- a. $1s, 2s$ b. $2p, 3p$ c. $3d_{xy}, 3d_{yz}$
d. $3s, 3d$ e. $4s, 5s$

Sol. For the electron present in the hydrogen orbital, the energy depends only upon the principal quantum number (n). Keeping this in mind, the orbital of higher energy in the given pairs is

- a. $2s$ b. $3p$ c. Same energy
d. Same energy e. $5s$

ILLUSTRATION 4.133

Answer the following:

- How many electrons can be filled in all the orbitals with $n+1 = 5$?
- Which of the two is paramagnetic: V(IV) or V(V) and why?
- How many unpaired electrons are present in Pd ($Z=46$)?
- The ion of an element has configuration $[\text{Ar}]3d^4$ in +3 oxidation state. What will be the electronic configuration of its atom?

Sol.

- $n+l=5$ has, $5s, 4p$, and $3d$ orbitals with two, six, and 10 electrons, respectively. Therefore, the total number of electrons is 18.
- The configurations are V(IV)— $[\text{Ar}]3d^1$ and V(V)— $[\text{Ar}]^{18}$. Therefore, V(IV) is paramagnetic in nature.
- The electronic configuration of the element palladium ($Z=46$) is $[\text{Kr}]364d^{10}5s^0$. Therefore, it has no unpaired electron.
- The configuration of ion is $[\text{Ar}]3d^4$. Therefore, the configuration of the atom is $[\text{Ar}]3d^5 4s^2$.

ILLUSTRATION 4.134

- For a d electron, the orbital angular momentum is
a. $\sqrt{6}\hbar$ b. $\sqrt{2}\hbar$ c. \hbar d. $2\hbar$
- If nitrogen atoms had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$ because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates

- Heisenberg's uncertainty principle
- Hund's rule
- Pauli's exclusion principle
- Bohr's postulate of stationary orbits

III. The less ground state electronic configuration of nitrogen atom can be represented by

- a.

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$
----------------------	----------------------	----------------------------

b.

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow$
----------------------	----------------------	------------------------------

c.

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\downarrow$
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d.

$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow\downarrow\downarrow$
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IV. For the energy levels in an atom, which of the following statements is/are correct?

- There are seven principal electron energy levels.
- The second principal energy level can have four sub-energy levels and contains a maximum of eight electrons.
- The M energy level can have a maximum of 32 electrons.
- The $4s$ sub-energy level is at a lower energy than the $3d$ sub-energy level.

Sol.

- I. a. For d electron, $l=2$,
orbital angular momentum

$$= \sqrt{l(l+1)} \hbar = \sqrt{2(2+1)} \hbar = \sqrt{6} \hbar$$

- c. According to Pauli's exclusion principle, an orbital cannot have more than two electrons and these two electrons have opposite spin.
- (a, d) In (a) and (d), the unpaired electrons have spins in the same direction. Hence, (a) and (d) are correct.
- (a, d) Statement (a) and (d) are true. Statement (b) is wrong because for $n=2$, $l=0, 1$ (two sub-energy levels). (c) is wrong because M shell means $n=3$. Maximum electrons it can have = $2n^2 = 2 \times 3^2 = 18$.
Hence, (a) and (d) are correct.

ILLUSTRATION 4.135

- Which of the following statements is/are correct?
a. The electronic configuration of Cr is $[\text{Ar}]3d^5 4s^1$ (atomic number of Cr = 24).
b. The magnetic quantum number may have a negative value.
c. In silver atom, 23 electrons have spin of one type and 24 of the opposite type (atomic number of Ag = 47).
d. The oxidation state of nitrogen in HN_3 is -3 .
- Many elements have non-integral atomic masses because
a. They have isotopes
b. Their isotopes have non-integral masses
c. Their isotopes have different masses
d. The constituents—neutrons, protons and electrons—combine to give rational masses

III. Which of the following is not correct for the electronic distribution in the ground state?

- a. $\text{Co} = [\text{Ar}] \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$
 b. $\text{Ni} = [\text{Ar}] \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$
 c. $\text{Cu} = [\text{Ar}] \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow$
 d. $\text{Zn} = [\text{Ar}] \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$

IV. The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^1$. This represents its

- a. Excited state b. Ground state
 c. Cationic form d. Anionic form

Sol.

I. (a, b, c) Only (d) is wrong because the oxidation state of N in HN_3 is $-1/3$.

Hence, (a), (b), and (c) are correct.

II. (a, c) Non-integral atomic masses are due to isotopes which have different masses.

Hence, (a) and (c) are correct.

III. c. $\text{Cu} = [\text{Ar}] \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow$

IV. b. The given electronic configuration is the ground state for chromium.

ILLUSTRATION 4.136

I. Which of the following sets of quantum numbers is/are not permitted?

- a. $n = 3, l = 3, m = 0, s = \frac{1}{2}$
 b. $n = 3, l = 2, m = 2, s = -\frac{1}{2}$
 c. $n = 3, l = 1, m = 2, s = -\frac{1}{2}$
 d. $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

II. Which of the following pairs of ions have the same electronic configuration?

- a. $\text{Cr}^{3+}, \text{Fe}^{3+}$ b. $\text{Fe}^{3+}, \text{Mn}^{2+}$
 c. $\text{Fe}^{3+}, \text{Co}^{3+}$ d. $\text{Se}^{3+}, \text{Cr}^{3+}$

III. Which of the following statements is correct?

- a. An orbital containing an electron having quantum numbers $n = 2; l = 0, s = +1/2$ is spherical.
 b. All photons have the same energy.
 c. The frequency of X-rays is less than that of radiowaves.
 d. As intensity of light increases, the frequency increases.

IV. Which of the following statements is/are not correct?

- a. The shape of an atomic orbital depends on the azimuthal quantum number.
 b. The orientation of an atomic orbital depends on the magnetic quantum number.

- c. The energy of an electron in an atomic orbital of a multi-electron atom depends on the principal quantum number.
 d. The number of degenerate atomic orbitals of one type depends on the values of principal, azimuthal, and magnetic quantum numbers.

Sol.

I. (a, c) When $n = 3, l$ cannot be 3; so (a) is not permitted. When $l = 1, m$ cannot be $+2$; so (c) is not permitted.

Hence, (a) and (c) are correct.

II. b. Fe^{3+} and Mn^{2+} have the same electronic configuration.

III. a. $l = 0$ or s orbital; the shape of s orbital is spherical.

IV. c. In a multi-electron atom, the energy of the electron not only depends upon n , but also on l, m , and some other factors also.

ILLUSTRATION 4.137

I. The Pauli exclusion principle applies to

- a. H b. H^{\oplus} c. H^{\ominus} d. None of these

II. Which of the following statements is/are true?

- a. One orbit can accommodate a maximum of two electrons.
 b. One sub-shell can accommodate a maximum of two electrons.
 c. One orbital can accommodate a maximum of two electrons.
 d. None of the above.

III. Which of the following is not according to the Pauli exclusion principle?

- a. $\uparrow\uparrow$ b. $\uparrow\downarrow$
 c. $\uparrow\downarrow \uparrow \uparrow$ d. (a) and (b) both

IV. Supposing that the Pauli exclusion principle is not correct, if one orbital can accommodate three electrons, what are the respective atomic numbers of the second member of alkali metal family and the first member of halogen family?

- a. 16, 14 b. 11, 9 c. 16, 9 d. 34, 17

Sol.

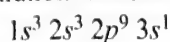
I. c. Since H has one electron and H^{\oplus} has no electron, the Pauli exclusion principle does not apply to them. However, H^{\ominus} has two electrons; hence, this principle applies on it.

II. c. An orbital can accommodate a maximum of two electrons having opposite spins.

III. d. The set of four quantum numbers is not same for the three electrons in answer (c). In answer (a), both electrons have the same set of quantum numbers, while in answer (b), the first and third electrons have the same set of quantum numbers.

IV. a. i. Sodium is the second member of alkali metal family.
 $\text{Na}^{11} = 1s^2 2s^2 2p^6 3s^1$

We know that the inner orbitals of sodium are fully filled and the outermost orbit has one electron. If inner orbitals can accommodate three electrons each, the configuration will be as follows:



Therefore, there will be 16 electrons in all. Hence, the atomic number will be 16.

- ii. The first member of halogen family is fluorine, F^9 , whose configuration is $1s^2 2s^2 2p^5$.

Halogen has one electron less than the next of inert noble gas. If inner orbitals can accommodate three electrons each, the configuration will be as follows:



Therefore, total number of electrons will be 14, and thus the atomic number will also be 14.

ILLUSTRATION 4.138

- I. Supposing that the Pauli exclusion principle is non-existent, which of the following is the most unacceptable configuration of Li in the ground state?

- a. $1s^2 2s^1$ b. $1s^3$
c. $1s^1 2s^2$ d. $1s^1 2s^1 2p^1$

- II. Which of the following should be correct according to Hund's rule?

- a. $C^6 = 1s^2 2s^2$ $\uparrow\uparrow$ \square \square
b. $O^8 = 1s^2 2s^2$ $\uparrow\downarrow$ $\uparrow\downarrow$ \square
c. $N^7 = 1s^2 2s^2$ $\uparrow\downarrow$ \uparrow \square
d. $F^9 = 1s^2 2s^2$ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow

- III. If the value of $n + l = 7$, then what should be the increasing order of energy of the possible sub-shells?

- a. $4f < 5d < 6p < 7s$ b. $7s < 6p < 5d < 4f$
c. $7s > 6p < 5d < 4p$ d. $4f < 5d < 6p > 7s$

- IV. Which of the following sub-shells will be filled by electrons after the orbital of the third principal shell is completely filled?

- a. $4s$ b. $4f$ c. $4d$ d. $4p$

- V. Which of the following should be the basis of entry of an electron in $4s$ orbital before $3d$ orbital?

- a. Energy level diagram b. Hund's rule
c. Pauli's principle d. Shielding constant

Sol.

- I. d. As a matter of fact, the configurations given in (b), (c) and (d) are wrong, but the configuration given in (d) is the most unacceptable because there is one electron in each of the three orbitals and according to the Pauli exclusion principle, a maximum of two electrons can be put in an orbital.
- II. d. Configuration of C^6 should be $2p_x^1 2p_y^1$ instead of $2p_x^2$. Configuration of O^8 should be $2p_x^2 2p_y^1 2p_z^1$ instead of $2p_x^2 2p_y^2$.

Configuration of N^7 should be $2p_x^1 2p_y^1 2p_z^1$ instead of $2p_x^2 2p_y^1$.

Configuration of F^9 , $2p_x^2 2p_y^2 2p_z^1$, is correct because two out of the three degenerate p orbitals are fully filled, one is half-filled, and there is no unfilled p orbital.

- III. a. $n + l = 7$

$$7 + 0 = 7s$$

$$6 + 1 = 6p$$

$$5 + 2 = 5d$$

$$4 + 3 = 4f$$

$$\text{Order of energy is } 4f < 5d < 6p < 7s$$

- IV. d. The electron goes to $4p$ after filling up $3d$.

- V. $n + l$ of $4s$ is $4 + 0 = 4$ and that of $3d$ is $3 + 2 = 5$. Therefore, the energy of $4s$ is lower than that of $3d$.

Increasing order of energy

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

The maximum number of electrons that can be accommodated in s orbital is 2, in p orbital is 6, in d orbital is 10, and in f orbital is 14.

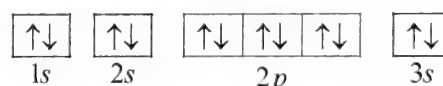
4.35 ELECTRONIC CONFIGURATION OF ATOMS

In an atom, electrons are distributed among various orbitals very much in accordance with rules governing the filling of different orbitals. This distribution of electrons into orbitals of an atom is called its electronic configuration.

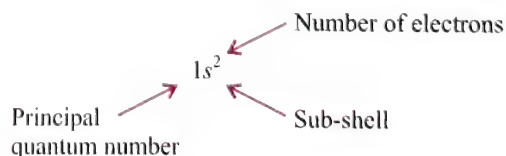
The electronic configuration of different atoms can be represented in two ways. For example,

- a. $1s^2 2s^2 2p^6 3s^2 \dots$ notation

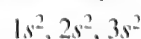
- b. Orbital diagram



In the first representation, the sub-shell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted in the superscript, i.e., for $1s^2$



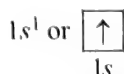
Similar sub-shells represented for different shells are differentiated by writing the principal quantum number before the respective sub-shell. For example,



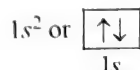
In the second representation, each orbital of the sub-shell is represented by a square or a circular box and the electron is represented by an upward arrow (\uparrow) for positive spin and by a downward arrow (\downarrow) a negative spin. The second notation has an advantage over the first notation as it represents all the four quantum numbers.

SOME EXAMPLES

1. *Hydrogen* (atomic number = 1): The hydrogen atom has only one electron; it must go to $1s$ orbital, which has the lowest energy. The electronic configuration of hydrogen atom is as follows:

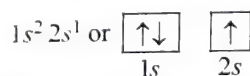


2. *Helium* (atomic number = 2): The helium atom has two electrons; the second electron can also go into $1s$ orbital (Pauli's principle). Its electronic configuration is as follows:

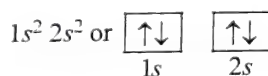


The two electrons differ from each other with opposite spin.

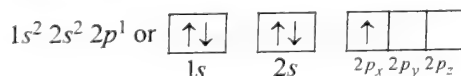
3. *Lithium* (atomic number = 3): Since lithium has three electrons and is not allowed to enter $1s$ orbital because of Pauli's exclusion principle, the third electron goes to the next lowest energy orbital, namely, $2s$. Thus, the electronic configuration of Li is as follows:



4. *Beryllium* (atomic number 4): The fourth electron in beryllium fills $2s$ orbital, therefore, electronic configuration is as follows:

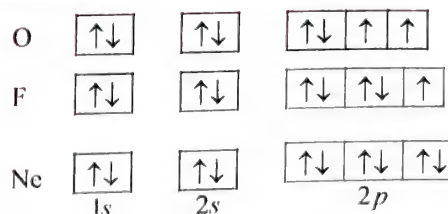
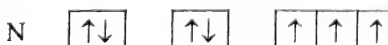
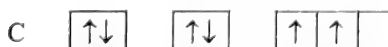
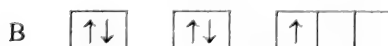
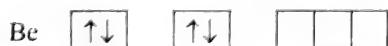


5. *Boron* (atomic number 5): In boron, there are five electrons; four electrons completely fill up $1s$ and $2s$ orbitals. The fifth electron goes to one of the $2p$ orbitals. Thus the configuration is as follows:



In the next five elements, carbon ($1s^2 2s^2 2p^2$), nitrogen ($1s^2 2s^2 2p^3$), oxygen ($1s^2 2s^2 2p^4$), fluorine ($1s^2 2s^2 2p^5$), and neon ($1s^2 2s^2 2p^6$), the $2p$ orbitals get progressively filled obeying Hund's rule of maximum multiplicity. This process is completed with the neon atom.

The orbital picture of these elements can be represented as follows:



The electronic configurations of elements from sodium (atomic number 11) to argon (atomic number 18) follow exactly the same pattern as the elements from lithium to neon, and $3s$ and $3p$ orbitals are also filled up with the same pattern. The $3p$ orbitals are completely filled up by the 19th electron in potassium (Atomic number 19), and the 20th electron in Ca (atomic number 20) enters the $4s$ orbital instead of $3d$ orbital because the energy of $4s$ orbital is lower than that of $3d$ orbital.

The electronic configurations of first 20 elements are given in Table 4.15.

Table 4.15 Electronic configuration of the first 20 elements

Atomic number	Elements	Orbital electronic configuration			
1	Hydrogen	$1s^1$			
2	Helium	$1s^2$			
3	Lithium	$1s^2$	$2s^1$		
4	Beryllium	$1s^2$	$2s^2$		
5	Boron	$1s^2$	$2s^2 2p_x^1$		
6	Carbon	$1s^2$	$2s^2 2p_x^1 2p_y^1$		
7	Nitrogen	$1s^2$	$2s^2 2p_x^1 2p_y^1 2p_z^1$		
8	Oxygen	$1s^2$	$2s^2 2p_x^2 2p_y^1 2p_z^1$		
9	Fluorine	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^1$		
10	Neon	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$		
11	Sodium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^1$	
12	Magnesium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2$	
13	Aluminium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1$	
14	Silicon	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1 3p_y^1$	
15	Phosphorus	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1 3p_y^1 3p_z^1$	
16	Sulphur	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^1 3p_z^1$	
17	Chlorine	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^1$	
18	Argon	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^2$	
19	Potassium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^2$	$4s^1$
20	Calcium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^2$	$4s^2$

The next 10 elements (atomic numbers 21 to 30) are scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn). The $3d$ orbital, being lower in energy than the $4p$ orbital, is filled first. All these elements are known as transition elements and $3d$ -series elements. For example, scandium (atomic number 21) has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$, the five $3d$ orbitals are progressively filled up till the last element of the series, that is, zinc (Atomic number 30). The electronic configuration of zinc is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$.

The electronic configurations of these 10 elements are given in Table 4.16.

Table 4.16 Electronic configuration of transition elements [scandium (atomic number 21) to zinc (atomic number 30)]

Atomic number	Element	Electronic configuration				
21	Scandium	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^1$	$4s^2$	
22	Titanium	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^2$	$4s^2$	
23	Vanadium	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^3$	$4s^2$	
24	Chromium	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^5$	$4s^1$	
25	Manganese	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^5$	$4s^2$	
26	Iron	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^6$	$4s^2$	
27	Cobalt	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^7$	$4s^2$	
28	Nickel	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^8$	$4s^2$	
29	Copper	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^1$	
30	Zinc	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2$	

It may be noted that in Table 4.16, chromium and copper have five and 10 electrons in $3d$ orbitals rather than four and nine because their position would have indicated two electrons in $4s$ orbitals. The reason for this ambiguity is that fully filled and half-filled orbitals have lower energy and thus have extra stability. Thus, $p^2, p^6, d^5, d^{10}, f^7, f^{14}$, etc., configurations, which are either fully filled or half-filled, are more stable (discussed in section 4.16). Therefore, chromium and copper have d^5 and d^{10} configurations.

As $3d$ orbitals get filled, the filling of $4p$ orbitals starts at gallium (Ga atomic number 31) and completes at krypton (Kr, atomic number 36). In the next 18 elements from rubidium (Rb) to Xenon (Xe), the pattern of filling $5s$, $4d$, and $5p$ orbitals is similar to that of $4s$, $3d$, and $4p$ orbitals. Then comes the turn of $6s$ orbitals. In caesium (Cs) and barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in $4f$ and $5d$ orbitals. After this, the filling of $6p$, then $7s$, and finally $5f$ and $6d$ orbitals takes place. Elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of known elements are tabulated in Table 4.17.

Table 4.17 Electronic configuration of elements

Atomic number	Symbol of element	Electronic configuration	Atomic number	Symbol of element	Electronic configuration
1	H	$1s^1$	39	Y	$[\text{Kr}]5s^2 4d^1$
2	He	$1s^2$	40	Zr	$[\text{Kr}]5s^2 4d^2$
3	Li	$[\text{He}]2s^1$	41	Nb	$[\text{Kr}]5s^1 4d^4$
4	Be	$[\text{He}]2s^2$	42	Mo	$[\text{Kr}]5s^1 4d^5$
5	B	$[\text{He}]2s^2 2p^1$	43	Tc	$[\text{Kr}]5s^1 4d^6$
6	C	$[\text{He}]2s^2 2p^2$	44	Ru	$[\text{Kr}]5s^1 4d^7$
7	N	$[\text{He}]2s^2 2p^3$	45	Rh	$[\text{Kr}]5s^1 4d^8$
8	O	$[\text{He}]2s^2 2p^4$	46	Pd	$[\text{Kr}]4d^{10}$
9	F	$[\text{He}]2s^2 2p^5$	47	Ag	$[\text{Kr}]5s^1 4d^{10}$

10	Ne	$[\text{He}]2s^2 2p^6$	48	Cd	$[\text{Kr}]5s^2 4d^{10}$
11	Na	$[\text{Ne}]3s^1$	49	In	$[\text{Kr}]5s^2 4d^{10} 5p^1$
12	Mg	$[\text{Ne}]3s^2$	50	Sn	$[\text{Kr}]5s^2 4d^{10} 5p^2$
13	Al	$[\text{Ne}]3s^2 3p^1$	51	Sb	$[\text{Kr}]5s^2 4d^{10} 5p^3$
14	Si	$[\text{Ne}]3s^2 3p^2$	52	Te	$[\text{Kr}]5s^2 4d^{10} 5p^4$
15	P	$[\text{Ne}]3s^2 3p^3$	53	I	$[\text{Kr}]5s^2 4d^{10} 5p^5$
16	S	$[\text{Ne}]3s^2 3p^4$	54	Xe	$[\text{Kr}]5s^2 4d^{10} 5p^6$
17	Cl	$[\text{Ne}]3s^2 3p^5$	55	Cs	$[\text{Xe}]6s^1$
18	Ar	$[\text{Ne}]3s^2 3p^6$	56	Ba	$[\text{Xe}]6s^2$
19	K	$[\text{Ar}]4s^1$	57	La	$[\text{Xe}]6s^2 5d^1$
20	Ca	$[\text{Ar}]4s^2$	58	Ce	$[\text{Xe}]6s^2 4f^2$
21	Sc	$[\text{Ar}]4s^2 3d^1$	59	Pr	$[\text{Xe}]6s^2 4f^3$
22	Ti	$[\text{Ar}]4s^2 3d^2$	60	Nd	$[\text{Xe}]6s^2 4f^4$
23	V	$[\text{Ar}]4s^2 3d^3$	61	Pm	$[\text{Xe}]6s^2 4f^5$
24	Cr	$[\text{Ar}]4s^1 3d^5$	62	Sm	$[\text{Xe}]6s^2 4f^6$
25	Mn	$[\text{Ar}]4s^2 3d^5$	63	Eu	$[\text{Xe}]6s^2 4f^7$
26	Fe	$[\text{Ar}]4s^2 3d^6$	64	Gd	$[\text{Xe}]6s^2 4f^7 5d^1$
27	Co	$[\text{Ar}]4s^2 3d^7$	65	Tb	$[\text{Xe}]6s^2 4f^9$
28	Ni	$[\text{Ar}]4s^2 3d^8$	66	Dy	$[\text{Xe}]6s^2 4f^{10}$
29	Cu	$[\text{Ar}]4s^1 3d^{10}$	67	Ho	$[\text{Xe}]6s^2 4f^{11}$
30	Zn	$[\text{Ar}]4s^2 3d^{10}$	68	Er	$[\text{Xe}]6s^2 4f^{12}$
31	Ga	$[\text{Ar}]4s^2 3d^{10} 4p^1$	69	Tm	$[\text{Xe}]6s^2 4f^{13}$
32	Ge	$[\text{Ar}]4s^2 3d^{10} 4p^2$	70	Yb	$[\text{Xe}]6s^2 4f^{14}$
33	As	$[\text{Ar}]4s^2 3d^{10} 4p^3$	71	Lu	$[\text{Xe}]6s^2 4f^{14} 5d^1$
34	Se	$[\text{Ar}]4s^2 3d^{10} 4p^4$	72	Hf	$[\text{Xe}]6s^2 4f^{14} 5d^2$
35	Br	$[\text{Ar}]4s^2 3d^{10} 4p^5$	73	Ta	$[\text{Xe}]6s^2 4f^{14} 5d^3$
36	Kr	$[\text{Ar}]4s^2 3d^{10} 4p^6$	74	W	$[\text{Xe}]6s^2 4f^{14} 5d^4$
37	Rb	$[\text{Kr}]5s^1$	75	Re	$[\text{Xe}]6s^2 4f^{14} 5d^5$
38	Sr	$[\text{Kr}]5s^2$	76	Os	$[\text{Xe}]6s^2 4f^{14} 5d^6$

4.35.1 ELECTRONIC CONFIGURATION IN CONDENSED FORM

The configuration of atom can also be written in condensed form by taking the configurations of noble gases as the core. The configuration of inert gases representing as core are written as $[\text{He}]^2$, $[\text{Ne}]^{10}$, $[\text{Ar}]^{18}$, $[\text{Kr}]^{36}$, $[\text{Xe}]^{54}$, and $[\text{Rn}]^{86}$.

For example, the electronic configuration of sodium (atomic number 11) can be written as $\text{Na} = [\text{Ne}]3s^1$

Electrons in completely filled shells are known as core electrons, and electrons that are added to the electronic shell with the highest principal quantum number are called *valence electrons*.

4.36 STABILITY OF COMPLETELY FILLED AND HALF-FILLED SUBSHELLS

The ground state electronic configuration of atom corresponds to the lowest energy state and gives higher stability. The electronic configuration of most of the atoms follows the basic rules. However, certain elements such as Cr or Cu do not follow the rules.

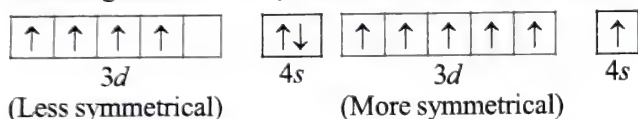
In such elements, the two sub-shells $4s$ and $3d$ slightly differ in energy, i.e., $4s$ is slightly lower in energy than $3d$ orbital. In

such case, the electron from lower energy sub-shell may jump to higher energy sub-shell provided such a shift results in all orbitals of the sub-shell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$, respectively, and not $3d^4 4s^2$ and $3d^9 4s^2$.

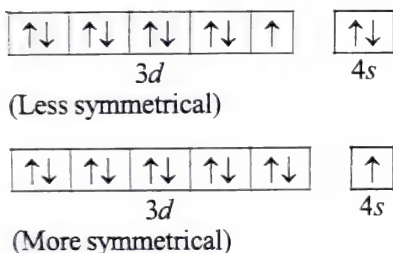
The extra stability of half-filled and fully filled electronic configuration can be explained in terms of symmetry and exchange energy.

a. Symmetrical distribution of electrons: The electronic configurations in which all the orbitals of the same sub-shell are either completely filled or half filled have relatively more symmetrical distribution of electrons. Consequently, their shielding of one another is relatively small and the electrons are more strongly attracted by the nucleus. This leads to more stability of the atom.

For example, the expected configuration of chromium is $3d^4 4s^2$. But shifting of one electron from $4s$ to $3d$ orbital makes the configuration more symmetrical and hence more stable.

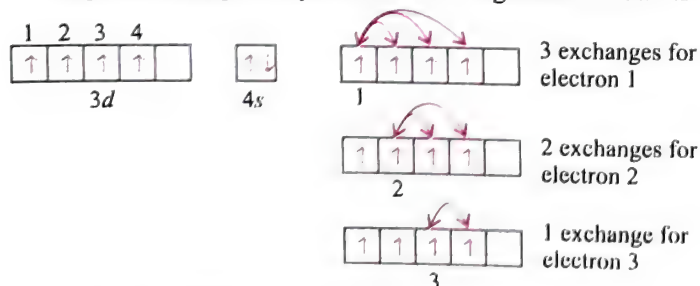


Similarly in copper, shifting of one electron from $4s$ to $3d$ makes the configuration more stable.



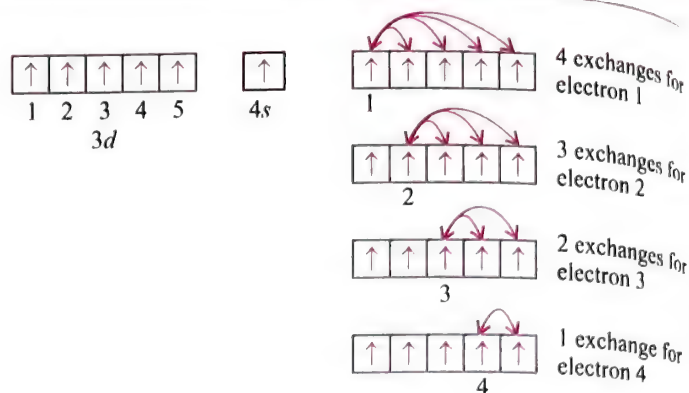
b. Exchange energy: Exchange means shifting of electrons from one orbital to another within the same sub-shell. Energy is released when electrons exchange their positions and is called the exchange energy. The maximum the number of exchanges, the maximum the energy released and the maximum the stabilisation. Half-filled and fully filled degenerate orbitals have more number of exchanges, and consequently, they have larger exchange energy of stabilisation.

For example, chromium atom with configuration $3d^5 4s^1$ has higher exchange compared to the configuration of $3d^4 4s^2$.



Total exchanges = $3 + 2 + 1 = 6$

Thus, in $3d^5$ arrangement, total electron exchanges are six, which implies that there are six possible arrangements with parallel spin in $3d^5$ configuration.



Total exchanges = $4 + 3 + 2 + 1 = 10$

It is clear from the above description that the total number of electron exchanges in $3d^6$ arrangement is larger, which gives it relatively greater stability.

To calculate the number of exchanges in a particular orbital, we can use the following mathematical expression:

$$\frac{n!}{2(n-2)!}$$

where n is the number of electrons in that sub-shell.

ILLUSTRATION 4.139

What will be the atomic number of an atom if its electronic configuration is $(n-2)s^2 (n-1)s^a p^b ns^2 p^2$ where $n = 3$, $a = 2$, and $b = 6$?

Sol. The electronic configuration is $(n-2)s^2 (n-1)s^a p^b ns^2 p^2$ and given that $n = 3$, $a = 2$, and $b = 6$.

On substituting all the values in the configuration, we get

$$(3-2)s^2 (3-1)s^2 p^6 3s^2 p^2 = 1s^2 2s^2 2p^6 3s^2 3p^2 = 14$$

Thus, the atomic number of the atom is 14.

ILLUSTRATION 4.140

What should be the number of electrons present in X^{2+} on the basis of electronic configuration if the ion X^{3-} has 14 protons?

Sol. X^{3-} has 14 protons, so, X also has 14 protons. Therefore, it has 14 electrons.

$$\therefore X = 14 = 1s^2 2s^2 2p^6 3s^2 3p^2$$

$$X^{2+} = 1s^2 2s^2 2p^6 3s^2 = 12 \text{ electrons}$$

ILLUSTRATION 4.141

I. An atom has 2K, 8L, and 5M electrons. Write its electronic configuration and indicate the following in it:

- Number of sub-shells
- Number of orbitals
- Number of unpaired electrons
- Number of electrons having $l = 1$

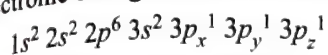
II. What atoms are indicated by the following configurations?

- $[\text{He}]2s^1$
- $[\text{Ne}]3s^2 3p^3$
- $[\text{Ar}]4s^2 3d^1$

III. Write the electronic configuration of the following and report the number of unpaired electrons in each case:

- Mn^{4+}
- Fe^{3+}
- Cr^{2+}
- Zn^{2+}

Sol. I. In the given atom, there are $2 + 8 + 5 = 15$ electrons. The electronic configuration of the atom is



- Number of sub-shells is 5.
- Number of orbitals is 9.
- Number of unpaired electrons is 3.
- Number of electrons having $l = 1$ is 9.

II. a. Li b. P c. Sc

III. a. Mn^{4+} ($Z = 25$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

b. Fe^{3+} ($Z = 26$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

c. Cr^{2+} ($Z = 24$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

d. Zn^{2+} ($Z = 30$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

ILLUSTRATION 4.142

I. The quantum numbers of the last electron of an element are given below. Predict the atomic number and name of the element from the following quantum numbers:

$$n = 3, l = 2, m = 0, s = -\frac{1}{2}$$

- a. 23, V b. 21, Sc c. 29, Cu d. 28, Ni

II. Predict the atomic number and element from the following

$$\text{quantum numbers: } n = 2, l = 1, m = -1, s = -\frac{1}{2}$$

- a. 5, B b. 8, O c. 6, C d. 7, N

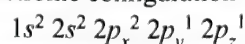
III. Write the electronic configuration of following species. Also find the number of unpaired electrons in each.

a. Fe, Fe^{2+} , Fe^{3+} (Z of Fe = 26)

b. Br, Br^- (Z of Br = 35)

c. V, V^{3+} (Z of V = 23)

Electronic configuration is



Atomic number = 8.

Element is oxygen.

III. Follow the order of increasing energy (aufbau rule):



a. Fe ($Z = 26$): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Note that 3d orbitals are not fully filled.



Orbitals filled as per Hund's rule.

Clearly, the number of unpaired electrons is 4.

• Fe^{2+} : ($Z = 26$) [Number of electrons = 24]

While writing the electronic configuration of cations, first write the configuration of neutral atom and then 'remove the desired number of electrons from the outermost orbital'.

In Fe^{2+} , remove $2e^-$ from $4s^2$ since 4s orbital (though lower in energy than 3d) is the outermost. Hence, the configuration of Fe^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$.

Note that the number of unpaired electrons remains same as that in Fe, i.e., 4.

• Fe^{3+} ($Z = 26$) [Number of electrons = 23]

Now remove $2e^-$ from $4s^2$ and $1e^-$ from $3d^6$ to get the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$.

Note that now all d orbitals have an odd electron (i.e., are half filled).



Hence, the number of unpaired electrons in Fe^{3+} is 5.

b. Br ($Z = 35$)

Following aufbau rule, the electronic configuration is: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$.

Clearly, one of the $4p^5$ orbitals contains unpaired electrons:



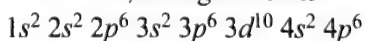
Orbitals filled as per Hund's rule

Hence, Br has only one unpaired electron.

• Br^- ($Z = 36$)

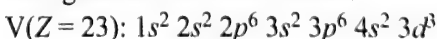
Since anion (s) is (are) formed by adding electron (s), so simply write the electronic configuration as per the total number of electrons finally.

For $Z = 36$, configuration is



Clearly, there are no unpaired electrons.

c. Following the pattern in (a), we can write the electronic configuration for V as follows:

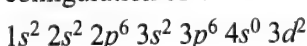


Orbitals filled as per Hund's rule

Three unpaired electrons

• V^{3+} ($Z = 20$)

Remove $3e^-$ from the outermost orbitals successively, i.e., $2e^-$ from $4s^2$ and $1e^-$ from $3d^3$. Hence, the electronic configuration of V^{3+} is



I. d.

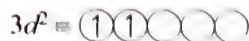
$n = 3$	$l = 2,$		$3d$		
$m = -2$	-1	0	+1	+2	
$d_{x^2-y^2}$	d_{yz}	d_{z^2}	d_{zx}	d_{xy}	
or	or	or	or	or	
d_{xy}	d_{zx}	d_{z^2}	d_{yz}	$d_{x^2-y^2}$	
↑	↑	↑	↑	↑	$s = +\frac{1}{2}$
↑↓	↑↓	↑↓			$s = -\frac{1}{2}$

Structure is $3d^8$ Atomic number = 28

The element is Ni.

II. b.

	$n = 2$	$l = 1,$	$2p$	
$m =$	-1	0	+1	
	p_x or p_y	p_z	p_y or p_x	
	↑	↑	↑	$s = +\frac{1}{2}$
	↑↓			$s = -\frac{1}{2}$



Orbitals filled as per Hund's rule

Two unpaired electrons.

ILLUSTRATION 4.143

- I. Which of the following is the number of electrons present in X^{2+} on the basis of electronic configuration if the ion X^3+ has 14 protons?
- a. 12 b. 14 c. 16 d. 18
- II. Which of the following is the electronic configuration of an atom in its first excited state if that atom is isoelectronic with O_2 ?
- a. $[Ne]3s^2 3p^4$ b. $[Ne] 3s^2 3p^3 3d^1$
 c. $[Ne]3s^1 3p^5$ d. None of these
- III. Which of the following is the electronic configuration of P in H_3PO_4 ?
- a. $[Ne]$ b. $[Ne] 3s^2 3p^6$
 c. $[Ne] 3s^2$ d. $[Ne] 3s^2 3p^1$
- IV. A neutral atom of an element has 2K, 8L, 9M, and 2N electrons. Find out the following:
- a. Atomic number
 b. Total number of s electrons
 c. Total number of p electrons
 d. Total number of d electrons
 e. Valency of the element
 f. Number of unpaired electrons

Sol.

- I. a. X^{2+} has 14 protons, i.e., X also has 14 protons and, therefore, 14 electrons.
 $X = 14 = 1s^2 2s^2 2p^6 3s^2 3p^2$
 $X^{2+} = 1s^2 2s^2 2p^6 3s^2 = 12$ electrons
- II. b. 16 electrons = $1s^2 2s^2 2p^6 3s^2 3p^4$
 (Two unpaired electrons)
 Excited state = $[Ne] 3s^2 3p^3 3d^1$
 (Four unpaired electrons)
- III. b. $[Ne] 3s^2 3p^6$
- IV. Electronic configuration of the neutral atom:
- $$\frac{1s^2}{K}, \frac{2s^2 2p^6}{L}, \frac{3s^2 3p^6 3d^1}{M}, \frac{4s^2}{N}$$
- a. Atomic number = Total number of electrons in neutral atom = 21
 b. Total number of s electrons = 8
 c. Total number of p electrons = 12
 d. Total number of d electrons = 1
 e. Valency of element = 2 and 3
 (due to number of electrons in outer shell and penultimate d sub-shell)
 f. Number of unpaired electrons = 1 (of 3d)

ILLUSTRATION 4.144

Write the electronic configuration of the following and report the number of unpaired electrons in each.

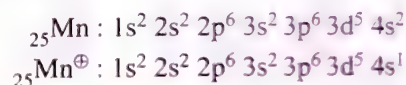
- a. Mn^{4+} b. Cr^{2+} c. Fe^{3+} d. Ni^{2+}
 e. $Cl^{(-)}$ f. Zn^{2+} g. Fe^{2+} h. Na
 i. Mg j. Cr^{3+}

Sol.

	Electronic configuration	Number of unpaired electron
a. ${}_{25}Mn^{4+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$	3
b. ${}_{24}Cr^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$	4
c. ${}_{26}Fe^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	5
d. ${}_{28}Ni^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$	2
e. ${}_{17}Cl^{(-)}$	$1s^2 2s^2 2p^6 3s^2 3p^6$	0
f. ${}_{30}Zn^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	0
g. ${}_{26}Fe^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	4
h. ${}_{11}Na$	$1s^2 2s^2 2p^6 3s^1$	1
i. ${}_{12}Mg$	$1s^2 2s^2 2p^6 3s^2$	0
j. ${}_{24}Cr^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$	3

Note: In case of writing the electronic configuration of cation, first write the configuration of the neutral atom and then take out the desired electrons from the outermost shell.

e.g.,

**ILLUSTRATION 4.145**

Write the four quantum numbers for V and VI electrons of carbon atom.

Sol. ${}_6C : 1s^2 2s^2 2p^2$

V electron	:	VI electron
$n = 2$		$n = 2$
$l = 1$		$l = 1$
$m = -1$ or $+1$		$m = 0$
$s = +\frac{1}{2}$ or $-\frac{1}{2}$		$s = +\frac{1}{2}$ or $-\frac{1}{2}$

ILLUSTRATION 4.146

I. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

- a. $n = 2$ $l = 1$ $m = -1$
 b. $n = 4$ $l = 2$ $m = 0$
 c. $n = 3$ $l = 1$ $m = \pm 1$
 d. $n = 4$ $l = 0$ $m = 0$
 e. $n = 3$ $l = 2$ $m = \pm 2$

II. ${}_4Be^1$ captures a K electron into its nucleus. What is the mass number and atomic number of the nuclide formed?

- III. a. An atomic orbital has $n = 3$. What are the possible values of l ?
 b. An atomic orbital has $l = 3$. What are the possible values of m ?

Sol.

- I. a. $\therefore n = 2$ and $l = 1 \therefore 2p$
 Also $m = -1 \therefore 2p_x$ or $2p_y$
 b. $4d_{z^2}$
 c. $3p_x$ or $3p_y$
 d. $4s$
 e. $3d_{x^2-y^2}$ or $3d_{xy}$
- II. ${}_4\text{Be}^{7+} + {}_{-1}\text{e}^0 \longrightarrow {}_3\text{Li}^7$
 \therefore Atomic number = 3; mass number = 7
- III. a. When $n = 3$, $l = 0, 1, 2$.
 b. When $l = 3$, $m = -3, -2, -1, 0, 1, 2, 3$.

ILLUSTRATION 4.147

- I. Using the s, p, d notation, describe the orbital with the following quantum numbers:
 a. $n = 1, l = 0$ b. $n = 2, l = 0$
 c. $n = 3, l = 1$ d. $n = 4, l = 2$
 e. $n = 4, l = 3$
- II. Using the Aufbau principle, write the electronic configuration for the grouped state of the following atoms: boron ($Z = 5$), neon ($Z = 10$), aluminium ($Z = 13$), chlorine ($Z = 17$), calcium ($Z = 20$), rubidium ($Z = 37$).
- III. The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. This represents its
 a. Excited state b. Ground state
 c. Cationic form d. Anionic form

Sol.

- I. a. $1s$ b. $2s$ c. $3p$ d. $4d$ e. $4f$
- II. a. Boron ($Z = 5$) $1s^2 2s^2 2p_x^1$
 b. Neon ($Z = 10$) $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
 c. Aluminium ($Z = 13$) $1s^2 2s^2 2p^6 3s^2 3p_x^1$
 d. Chlorine ($Z = 17$) $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
 e. Calcium ($Z = 20$) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
 f. Rubidium ($Z = 37$) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
- III. b. Ground state, because half-filled d orbital is more stable.

4.37 SPHERICAL (OR RADIAL) NODES AND NODAL PLANES

- a. **Spherical node:** The spherical surface where the probability of finding an electron is zero is called a **spherical node** or **radial node**.

In general, number of spherical nodes in an orbital = $n - l - 1$, where n is the principal quantum number and l is the azimuthal quantum number. For example,

- i. For $1s$, $n = 1$ and $l = 0$
 \therefore No. of spherical nodes = $1 - 0 - 1 = 0$
- ii. For $2s$, $n = 2$ and $l = 0$
 \therefore No. of spherical nodes = $2 - 0 - 1 = 1$
- iii. For $2p$, $n = 2$ and $l = 1$
 \therefore No. of spherical nodes = $2 - 1 - 1 = 0$

- iv. For $3s$, $n = 3$ and $l = 0$

$$\therefore \text{No. of spherical nodes} = 3 - 0 - 1 = 2$$

- v. For $3p$, $n = 3$ and $l = 1$

$$\therefore \text{No. of spherical nodes} = 3 - 1 - 1 = 1$$

- b. **Nodal plane:** The plane in which the probability of finding an electron is zero is called a **nodal plane**. Number of nodal planes for an orbital = l . For example, (i) s -orbital ($l = 0$) has no nodal plane, (ii) p -orbital ($l = 1$) has one nodal plane, (iii) d -orbital ($l = 2$) has two nodal planes and (iv) f -orbital ($l = 3$) has three nodal planes.

- c. **Total number of nodes** = $n - 1$

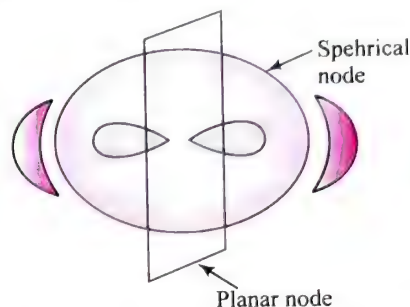


Fig. 4.32 Spherical nodes and nodal plane in 3p-orbital

4.38 ORBITAL WAVE FUNCTIONS, PROBABILITY DISTRIBUTION, AND SHAPE OF ORBITALS

An atomic orbital is a one-electron wave function $\psi(r, \theta, \phi)$ obtained from the solution to the Schrödinger equation for the hydrogen atom. It is a mathematical function of the three coordinates of the electron (r, θ, ϕ) and can be factorised into three separate parts each of which is a function of only one coordinate:

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

where $R(r)$ is the radial function which gives the dependence of orbital upon the distance r of the electron from the nucleus and $\Theta(\theta)$ and $\Phi(\phi)$ are the angular functions giving the angular dependence of orbital on θ and ϕ , respectively. Further, the radial function depends upon the quantum numbers n and l , whereas the angular part depends upon the quantum numbers l and m_l and is independent of n . The total wave function ψ may, therefore, be more explicitly written as

$$\psi(r, \theta, \phi) = \underset{\text{Radial part}}{R_{n,l}(r)} \underset{\text{Angular part}}{\Theta_{l,m}(\theta) \Phi_m(\phi)}$$

The orbital wave function ψ has no physical significance. It is the square of the absolute value of the orbital wave function $|\psi|^2$ which has a physical significance—it measures the electron probability density at a point in an atom. It would, therefore, be interesting to know how ψ and $|\psi|^2$ vary as a function of the three coordinates r, θ , and ϕ for different orbitals. Such a representation of the variations of ψ or $|\psi|^2$ in space would, however, need a four-dimensional graph—three dimensions for the coordinates and the fourth for ψ or $|\psi|^2$. It is not possible to show such a variation in a single diagram since we can draw only two-dimensional diagrams on paper. We can get around this difficulty by drawing

separate diagrams for (i) variation of radial function and (ii) angular function.

4.38.1 VARIATIONS OF RADIAL WAVE FUNCTION R

a. Plots of radial wave function R against the distance r :

The variation of the radial part of the orbital wave functions for $1s$, $2s$, and $2p$ orbitals is given in Fig. 4.33. In all these cases, R approaches zero as r approaches infinity. In $2p$ orbital plot, one can observe that the radial function value changes from positive to zero then to negative. The region where this function reduces to zero is called nodal surfaces or simply nodes. In general, it has been found that ns orbital has $(n - 1)$ nodes, that is the number of nodes increases with an increase in the principal quantum number n , i.e., number of nodes for $2s$ is one and for $3s$ is two and so on. The importance of these plots is that it gives information about how the radial wave function changes with distance r and also about the presence of nodes where the change of sign of R occurs.

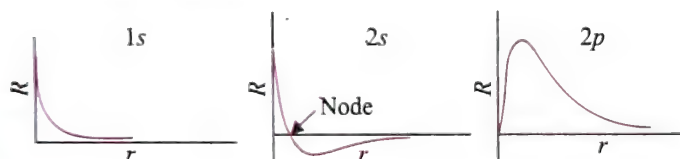


Fig. 4.33 Plots between R and r

b. Radial probability density (R^2):

The square of the radial wave function, R^2 , is the measure of the probability of finding the electron in a unit volume around a particular point and is called probability density.

The plots in Fig. 4.34 inform us about the probability density or relative electron density at a point as a function of radius. It is observed that for s orbitals, the maximum electron density is at the nucleus, while all other orbitals have zero electron density at the nucleus. For $1s$ orbital, probability density decreases sharply as we move away from the nucleus. On the other hand, for $2s$ orbital it first decreases sharply to zero (nodal point or node) and again starts increasing.

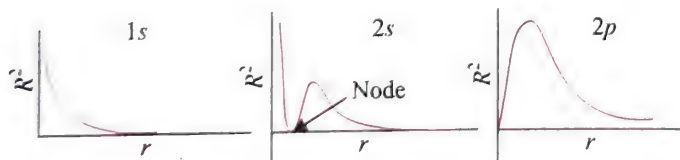


Fig. 4.34 Plots of R^2 against r (atomic radius) for $1s$, $2s$, and $2p$ orbitals

c. Radial distribution function, ($4\pi r^2 R^2$):

The radial density R^2 for an orbital, as discussed above, gives the probability density of finding the electron at a point at a distance r from the nucleus. Since the atoms have spherical symmetry, it is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radii $r + dr$ and r .

Thus, the radial probability is the probability of finding the electrons in a small spherical shell around the nucleus at a particular distance from it.

Volume of small shell

$$= (\text{Volume of bigger sphere}) - (\text{Volume of smaller sphere})$$

$$= \frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi(r^3 + dr^3 + 3r^2 dr + 3r dr^2) - \frac{4}{3}\pi r^3$$

As dr is very small, so its higher power can be neglected. Thus, the above equation becomes

$$\begin{aligned} & \frac{4}{3}\pi(r^3 + 3r^2 dr) - \frac{4}{3}\pi r^3 \\ &= \frac{4}{3}\pi r^3 + 4\pi r^2 dr - \frac{4}{3}\pi r^3 = 4\pi r^2 dr \end{aligned}$$

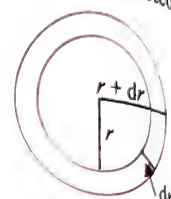


Fig. 4.35

Thus, radial probability $= 4\pi r^2 dr \psi^2$

The radial probability function ($4\pi r^2 R^2$) gives the probability of finding the electron at a distance r from the nucleus regardless of direction.

The radial probability distribution curves obtained by plotting radial probability functions versus distance r from the nucleus for $1s$, $2s$, and $2p$ orbitals are shown in Fig. 4.34.

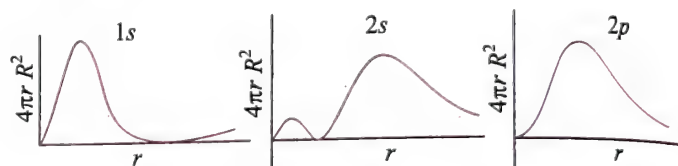


Fig. 4.36 Plots of $4\pi r^2 R^2$ against r (atomic radius) for $1s$, $2s$ and $2p$ orbitals

The important features of these plots are discussed below:

$1s$ orbital:

The radial probability function for $1s$ orbital initially increases with an increase in distance from the nucleus. It reaches a maximum at a distance very close to the nucleus and then decreases. The maximum in the curve corresponds to the distance at which the probability of finding the electron is maximum. This distance is called the radius of maximum probability and for hydrogen atom has a value of 52.9 pm.

It may be noted that while Bohr's model restricts the electron to a definite orbit at a fixed distance from the nucleus, the quantum mechanical model gives merely the maximum probability of finding the electron at 52.9 pm distance from the nucleus. In case of hydrogen atom, according to Bohr's model, the electron always stays at a distance of 52.9 pm from the nucleus. According to the quantum mechanical model, however, the electron in the hydrogen atom can be at any distance but, the most probable distance for finding the electron is 52.9 pm.

$2s$ and $2p$ orbitals:

The radial probability function curve for $2s$ orbital shows two maxima—a smaller one near the nucleus and a bigger one at a larger distance. In between these two maxima, it passes through a zero value indicating that there is zero probability of finding the electron at that distance. The point at which the probability of finding the electron is zero is called a nodal point.

The distance of maximum probability for a $2p$ electron is slightly less than that for a $2s$ electron. However, in contrast to $2p$

curve, there is a small additional maximum in the $2s$ curve. This indicates that the electron in $2s$ orbital spends some of its time near the nucleus. In other words, the $2s$ electron penetrates a little closer to the nucleus and is, therefore, held more tightly than the $2p$ electron. That is the reason why the $2s$ electron is more stable and has lower energy than the $2p$ electron.

4.38.2 PLOTS OF ANGULAR WAVE FUNCTION ' $\Theta\Phi$ '

As already mentioned, the angular wave function ' $\Theta\Phi$ ' depends only on the quantum numbers l and m_l and is independent of the principal quantum number n for a given type of orbital. It therefore means that all s orbitals will have same angular wave function. The plots of the angular wave function ' $\Theta\Phi$ ' and angular probability density $|\Theta\Phi|^2$ for s and p_z orbitals are shown in Fig. 4.37(a, b). Let us discuss both these plots separately.

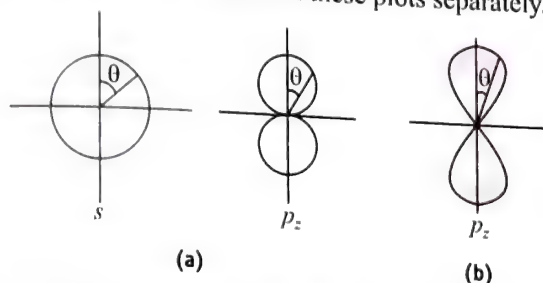


Fig. 4.37 (a) Angular part of the wave function for hydrogen-like s orbitals and p_z orbital, and (b) angular probability function for p_z orbital. Only two dimensions of the three-dimensional function have been shown

a. Angular wave function $\Theta\Phi$ [Fig. 4.37(a)]: For an s orbital, the angular part is independent of angle and is, therefore, of constant value. Hence, this graph is circular or, to be precise it is spherical in three dimensions. For the p_z orbital, we get two tangent spheres. The p_x and p_y orbitals are identical in shape but are oriented along the x - and y -axes, respectively. The angular wave function plots for d and f orbitals are four-lobed and six-lobed, respectively.

It is necessary to keep in mind that in the angular wave function plots, the distance from the centre is proportional to the numerical values of ' $\Theta\Phi$ ' in that direction and is not the distance from the centre of the nucleus.

b. Angular probability density $|\Theta\Phi|^2$ [Fig. 4.37(b)]: The angular probability density plots can be obtained by squaring the angular function plots shown in Fig. 4.37(a). On squaring, different orbitals change in different ways. For an s orbital, the squaring causes no change in shape since the function is same everywhere; thus another sphere is obtained. For both p and d orbitals, however, the plot tends to become more elongated on squaring as shown for p_z in Fig. 4.37(b).

4.38.3 PLOTS OF TOTAL PROBABILITY DENSITY: SHAPES OF ATOMIC ORBITALS

The problems associated with the representations of the variations of $|\psi|^2$ in space have been circumvented by the following two approaches:

a. Boundary surface diagrams: The shape of the orbitals can be represented quite accurately with the help of boundary surface diagrams. In this representation, a boundary surface

(contour surface) is drawn in space for an orbital on which the value of probability density (ψ^2) is constant.

A boundary surface that encloses the regions of maximum probability (say 90%) best describes the shape of orbitals. It is not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. It is because the probability density $|\psi|^2$ always has some value, however small it may be, at any finite distance from the nucleus. The boundary surface diagrams for $1s$ and $2s$ orbitals are given in Fig. 4.38.

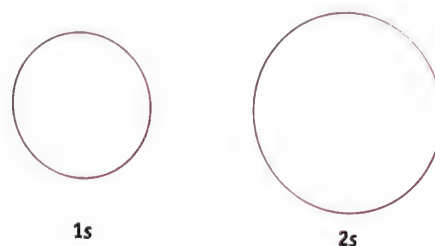


Fig. 4.38 Boundary surface diagrams for $1s$ and $2s$

The boundary surface diagrams for s orbitals are spherical in shape, i.e., the probability of finding the electron at a given distance is equal in all directions. The size of the s orbitals increases with increase in n , that is $4s > 3s > 2s > 1s$, and the electron is located further away from the nucleus as the principal quantum number increases. Boundary surface diagrams for three $2p$ orbitals ($l = 1$) are shown in Fig. 4.39.

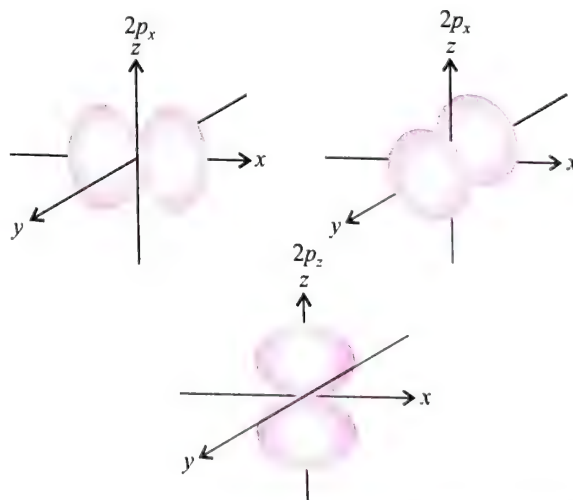


Fig. 4.39 Boundary surface diagrams for three $2p$ orbitals

The diagrams are not spherical. Each p orbital consists of two sections called lobes that are on the either side of the plane that passes through the nucleus. The three $2p$ orbitals lie along x -, y - and z -axes, respectively, and are designated as $2p_x$, $2p_y$, and $2p_z$. The three p orbitals are identical in shape, size, and energy, but they differ only in orientation. Like s orbital, p orbitals increase in size and energy with an increase in the principal quantum number as $4p > 3p > 2p$.

The boundary surface diagram for d orbital is shown in Fig. 4.40. The five d orbitals are designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, and d_{z^2} . The shape of the first four d orbitals are similar to each other, whereas the fifth one d_{z^2} is different from other orbitals.

The d orbitals for which n is greater than 3 ($4d$, $5d$) also have shapes similar to $3d$ orbitals but differ in energy and size.

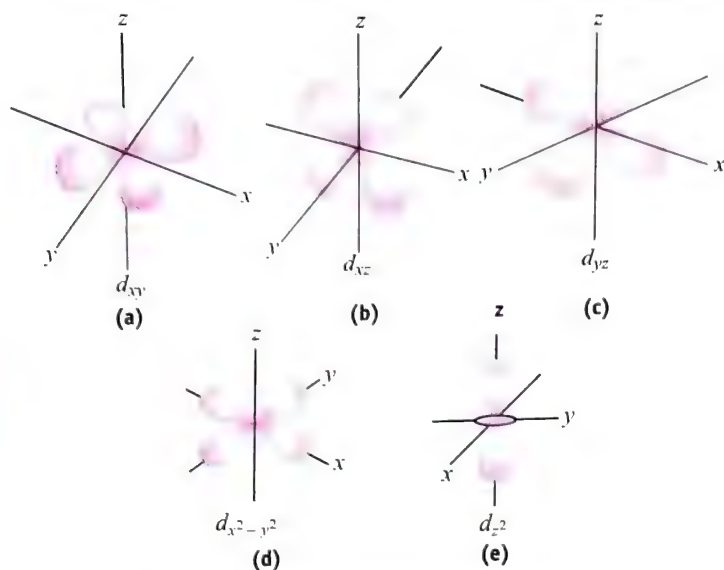


Fig. 4.40 Boundary surface diagrams for five $3d$ orbitals

b. Charge cloud diagrams: This is an alternative way to describe probability $(\psi)^2$ in terms of negative charge cloud. The charge cloud is represented by small dots, and the probability of finding the electron in a particular region of space is directly proportional to the density of such orbits in that regions. The charge cloud diagrams of $1s$, $2s$, and $3s$ orbitals are shown in Fig. 4.41.

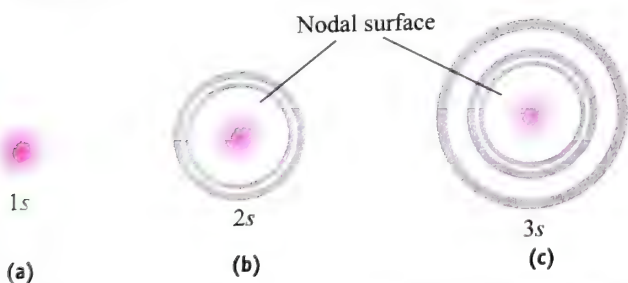


Fig. 4.41 Charge cloud diagram of (a) $1s$ orbital, (b) $2s$ orbital, and (c) $3s$ orbital

For p -orbitals, there are three possible orientations of electron cloud. These three orientations or orbitals of a p sub-shell are designated as p_x , p_y , and p_z or p_{+1} , p_{-1} , and p_0 , respectively. p_x , p_y , and p_z orbitals are oriented along x -axis, y -axis, and z -axis, respectively. Each p orbital has two lobes, which are separated by a plane of zero probability called *nodal plane*. Each p orbital is, thus, *dumb-bell shaped*. The spatial distribution of $2p$ orbitals is shown in Fig. 4.42.

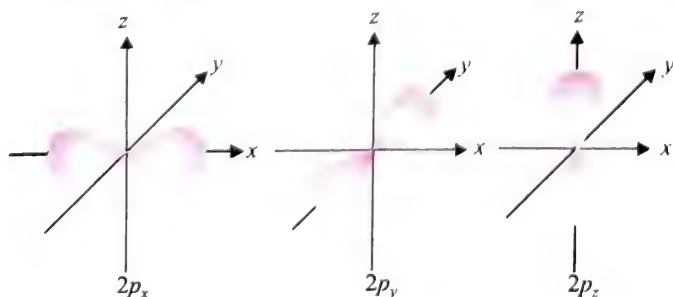


Fig. 4.42 $2p$ orbitals

In the absence of an external electric or magnetic field, the three p orbitals of a particular energy level have same energy. Such orbitals having equal energy are called *degenerate orbitals*. In the presence of external magnetic or electric field, this degeneracy is lost because the three p orbitals are oriented differently with respect to applied field.

The charge cloud picture of the five $3d$ orbitals is given in Fig. 4.43.

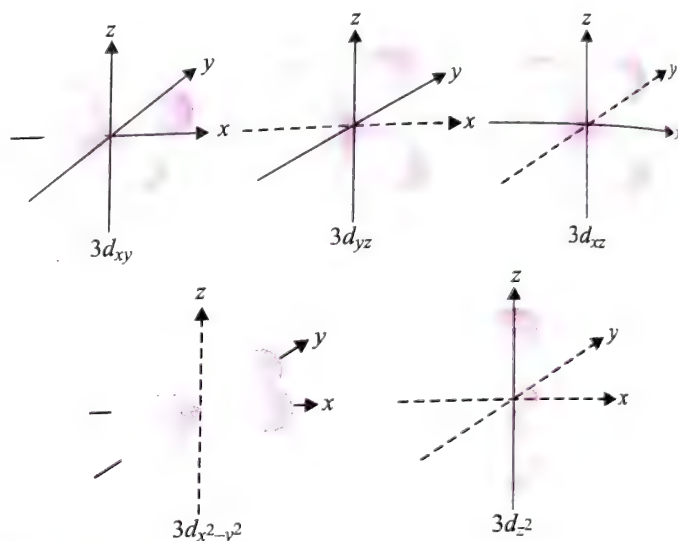


Fig. 4.43 The five $3d$ orbitals

ILLUSTRATION 4.148

The nucleus of an atom is located at $x = y = z = 0$.

- If the probability of finding an s orbital electron in a tiny volume around $x = a$, $y = z = 0$ is 1.0×10^{-5} , what is the probability of finding the electron in the same sized volume around $x = z = 0$, $y = a$?
- What will be the probability at the second site if the electron is in p_z orbital? Explain.

Sol.

- The distance of s orbitals, 1.0×10^{-5} , is the same for two volumes (i.e., $x = a$, $y = a$, $a = 1.0 \times 10^{-5}$) and the s orbital is spherically symmetrical. Hence, the probability of finding the electron in each of two volumes is same.
- Since the p_z orbital has a node at $z = 0$, the probability of finding the electron in this volume is zero.

ILLUSTRATION 4.149

- Which of the d orbitals lies in the xy -plane?
 - d_{xz}
 - d_{xy}
 - $d_{x^2-y^2}$
 - d_{xy} and $d_{x^2-y^2}$
- Suggest the angular and spherical nodes in the followings:
 - $3p$
 - $3d$
 - $2s$
 - $3s$
- The wave function ψ in the Schrödinger wave equation represents
 - Probability of the electron

- b. Amplitude of the wave
c. Frequency of the wave
d. Speed of the wave

Sol. I. c. The $d_{x^2-y^2}$ orbital lies in the xy -plane.

II. Angular nodes = l (azimuthal quantum number)

Spherical node = $n - l - 1$

- a. 1, 1 b. 2, 0 c. 0, 1 d. 0, 2

III. b.

ILLUSTRATION 4.150

The wave function of $3s$ electron is given by

$$\psi_{3s} = \frac{1}{81\sqrt{3}\pi} \left(\frac{1}{a_0}\right)^{3/2} \left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^3 \right] e^{-r/3a_0}$$

It has a node at $r = r_0$. Find the relation between r_0 and a_0 .

Sol. At nodal point, $\psi = 0$. From the given wave function, we find that $\psi = 0$ at following values of r :

$$\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^3 \right] = 0$$

Solving for r_0/a_0 , we get

$$\frac{r_0}{a_0} = \frac{18 \pm \sqrt{18^2 - 216}}{4} = \frac{18 \pm 10.4}{2}$$

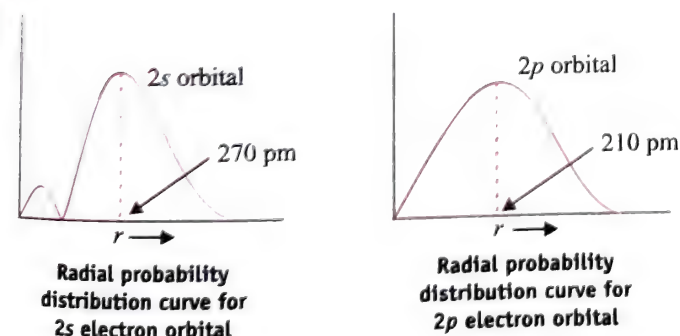
Hence $r = 14.2a_0$ and $r_0 = 3.9a_0$

Besides there is a node at $r = \infty$.

ILLUSTRATION 4.151

Draw the radial probability distribution curves for $2s$ and $2p$ electron orbitals and compare them.

Sol. The radial probability distribution curves for $2s$ and $2p$ electron orbitals are given below:



Comparison of radial probability distribution curves for $2s$ and $2p$ electron orbitals: The following points are noteworthy when we compare the radial probability curves for different electron orbitals:

- a. The radial probability distribution curve for $2s$ electron orbital shows two maxima—a smaller one near the nucleus and a bigger one away from it at a larger distance. In between two maxima, there is one minimum

where the probability of finding the electron is almost at the nodal point.

- b. Although the radius of maximum probability for $2p$ electron (210 pm) is slightly less than that for $2p$ electron (270 pm), because of the presence a small additional maxima, $2s$ electron spends some more time near the nucleus than $2p$ electron. In other words, $2s$ electron is held more tightly by the nucleus than $2p$ electron. This is what we actually observe.

ILLUSTRATION 4.152

In all, how many nodal planes are there in the atomic orbitals for the principal quantum number $n = 3$?

Sol. Shell with $n = 3$ has $1s$ ($3s$), $3p$ (p_x, p_y, p_z), and $5d$ ($d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$, and d_{z^2}) orbitals.

- s has no nodal plane.
- Each of p_x, p_y, p_z has one nodal plane, which means a total of three nodal planes.
- d_{z^2} has no nodal plane

Each of $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$ has two nodal planes, which means a total of eight nodal planes.

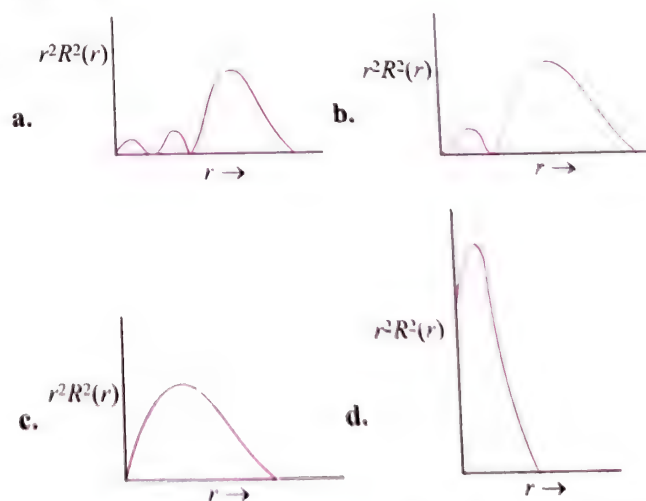
Hence, for $n = 3$, a total of 11 nodal planes are there.

ILLUSTRATION 4.153

I. Choose the correct statements from among the following:

- A node is a point in space where the wave function (ψ) has zero amplitude.
- The number of peaks in radial distribution is $n - 1$.
- Radial probability density $\pi_{n,l}(r) = 4\pi r^2 R_{n,l}^2(r)$.
- ψ^2 represents the atomic orbital.

II. Which of the following radial distribution graphs corresponds to $l = 2$ for H atom for the least value of n for which $l = 2$ is allowed?



III. For an electron in a hydrogen atom, the wave function ψ is proportional to $\exp(-r/a_0)$, where a_0 is the Bohr's radius. What is the ratio of the probability of finding the electron at the nucleus to the probability of finding it at a_0 ?

- a. e b. $1/e^2$ c. e^2 d. 0

- IV. The wave function of atomic orbital of H-like atoms is given as under:

$$\psi_{2s} = \frac{1}{4\sqrt{2}\pi} Z^{3/2} (2 - Zr) e^{-Zr/2}$$

Given that the radius is in Å, then which of the following is the radius for nodal surface for He^{\oplus} ion?

- a. 1 au b. 2 au c. 2.5 au d. 4 au

(au = atomic unit of radius)

Sol.

- I. (a, b, c) (Factual statement)
(d) is wrong as ψ represents atomic orbitals, ψ^2 represents probability and density.
- II. c. Option (c) represents the distribution of $l = 2$ for H atom.
a. Two nodes: $(n - l - 1) = 2$, $(n - 2 - 1) = 2$
 $\therefore n = 5$ (High value of n)
b. One node: $(n - 2 - 1) = 1$, $n = 4$.
c. Zero node: $(n - 2 - 1) = 0$, $n = 3$. (Minimum value of n which $l = 2$ is allowed)
d. Graph does not correspond to any radial distribution curve.
- III. d. Because probability at $s = a_0$ is proportional to $e^{-2s/a_0} = e^{-2}$
 $[\because P = |\psi|^2 \propto (e^{-s/a_0})^2]$
Probability at nucleus = 0
- IV. a. $(2 - Zr) = 0$ ($\because Z = 2$ for He^{\oplus})
 $\therefore Zr = 2$
 $r = \frac{2}{Z} = \frac{2}{2} = 1 \text{ au}$

ILLUSTRATION 4.154

- I. Suggest the angular and spherical nodes in
a. $4p$ b. $3p$ c. $3s$
- II. The correct Schrödinger wave equation for an electron with E as total energy and V as potential energy is
a. $\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2}{mh^2} (E - V)\psi = 0$
b. $\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi m}{h^2} (E - V)\psi = 0$
c. $\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$
d. $\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi m^2}{h} (E - V)\psi = 0$
- III. In an atomic orbital, the sign of lobes indicates the
a. Sign of the probability distribution
b. Sign of charge
c. Sign of the wave function
d. Presence or absence of electron
- IV. The permissible solution to the Schrödinger wave equation gave an idea of quantum numbers.
a. 4 b. 2 c. 3 d. 1

Sol.

- I. Angular nodes = l , spherical node = $n - l - 1$
a. 1, 2 b. 1, 1 c. 0, 2
- II. c. $\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$
- III. c. Sign of wave function
- IV. c. 3 (n, l, m)

ILLUSTRATION 4.155

- I. Which of the following d-orbitals has dough-nut shape?
a. d_{xy} b. d_{yz} c. $d_{x^2-y^2}$ d. d_{z^2}
- II. The number of nodal planes d orbital has
a. Zero b. One c. Two d. Three
- III. The energy of state s_1 in units of the hydrogen atom ground state energy is
a. 0.75 b. 1.50 c. 2.25 d. 4.50

Sol.

- I. d. d_{z^2}
- II. c. Two
- III. c.
Spherically symmetrical state (i.e., s orbital) with one radial node = $2s = s_1$
 $(n - l - 1)$
 $n = 2 \longrightarrow s_2$ (one radial node)
 $\equiv n_2$
and $(E_n)_{\text{Li}^{2+}} = (E)_{\text{H}}$
 $\Rightarrow -13.6 \times \frac{3^2}{n_2^2} = -13.6 \times \frac{1^2}{1^2}$
 $\Rightarrow n_2 = 3$
 $\Rightarrow s_2 = 3p$
 $\Rightarrow \frac{E_{s_1}}{(E_{\text{H}})_{n=1}} = \frac{-13.6 \times \frac{3^2}{2^2}}{-13.6 \times \frac{1^2}{1^2}} = 2.25$

CONCEPT APPLICATION EXERCISE 4.2

Subjective Type

- How many quantum numbers are needed to designate an orbital? Name them.
- The principal quantum number n of an atomic orbital is 5. What are the possible values of l ?
- The azimuthal quantum number l of an orbital is 3. What are the possible values of m ?
- What is the lowest value of n that allows g orbitals to exist?
- Give the notation for the sub-shells denoted by the following quantum numbers:
a. $n = 5, l = 2$ b. $n = 6, l = 3$
c. $n = 4, l = 0$ d. $n = 5, l = 4$
- How many electrons in a fully filled f sub-shell have $m_l = 0$?
- An electron is in one of the $3d$ orbitals. Give the possible values of n, l , and m_l for this electron.

8. If the largest value of m_l for an electron is +3, in what type of subshell the electron may be present?
 9. Explain, giving reasons, which of the following sets of quantum numbers are not possible.

a. $n=0$ $l=0$ $m_l=0$ $m_s=+1/2$

b. $n=1$ $l=0$ $m_l=0$ $m_s=-1/2$

c. $n=1$ $l=1$ $m_l=0$ $m_s=+1/2$

d. $n=2$ $l=1$ $m_l=0$ $m_s=-1/2$

e. $n=3$ $l=3$ $m_l=-3$ $m_s=+1/2$

f. $n=3$ $l=1$ $m_l=0$ $m_s=+1/2$

10. How many electrons in an atom may have the following quantum numbers?

a. $n=4, m_s=-\frac{1}{2}$ b. $n=3, l=0$

11. How many orbitals are possible in
 a. 4th energy level b. 5f sub-shell

12. What are the possible values of m_l for the different orbitals of
 a. p sub-shell b. d sub-shell

13. What is the shape of 2s orbital? Give two points of difference between 1s and 2s orbitals.

14. a. How many sub-shells are associated with $n=4$?
 b. How many electrons will be present in the sub-shells having m_s value of $-1/2$ for $n=4$?

15. How many spherical nodal surfaces are there in
 a. a 3s orbital b. a 3p orbital

Objective Type

16. The principal quantum number represents
 (1) Shape of an orbital
 (2) Number of electrons in an orbit
 (3) Distance of an electron from the nucleus
 (4) Orientation of orbitals in space
17. The energy of an electron of $2p_y$ orbital is
 (1) Greater than $2p$ orbital
 (2) Less than $2p_z$ orbital
 (3) Equal to $2s$ orbital
 (4) Same as that of $2p_x$ and $2p_z$ orbitals
18. The orbital angular momentum of an electron in 2s orbital is
 (1) 4 (2) 1 (3) 0 (4) $\frac{h}{2\pi}$
19. The number of nodal planes (planes of zero electron density) in the d_{xy} orbital is
 (1) 1 (2) 2 (3) 0 (4) 4

ANSWERS

Subjective Type

1. 3
 2. Possible values of l are 0, 1, 2, 3 and 4
 3. Possible values of m are +3, +2, +1, 0, -1, -2, -3
 4. $n=5$ 6. 2 11. a. 16 b. 7

12. a. +1, 0, -1 b. +2, +1, 0, -1, -2

15. a. Two b. One

Objective Type

16. (3) 17. (4) 18. (3) 19. (2)

Solved Examples

Level-I

EXAMPLE 4.1

- a. What is the shape of
 i. s orbital ii. p orbital
 b. Which of the following orbitals are spherically symmetrical?
 i. p_x ii. s iii. P_y

Sol.

- a. i. The shape of s orbital is spherically symmetrical. The size of a s orbital depends upon the principal quantum number n . The size of s orbital belonging to the second principal quantum number is bigger than the first.
 ii. A p orbital is double shaped whose lobes point along x-, y- or z-axes.
 b. s orbital

EXAMPLE 4.2

From the following sets of quantum numbers, state which are possible. Explain why the others are not permitted?

- a. $n=0, l=0, m=0, s=+1/2$
 b. $n=1, l=0, m=0, s=-1/2$
 c. $n=1, l=1, m=0, s=+1/2$
 d. $n=1, l=0, m=+1, s=+1/2$
 e. $n=0, l=1, m=-1, s=-1/2$
 f. $n=2, l=2, m=0, s=-1/2$
 g. $n=2, l=1, m=0, s=-1/2$

Sol.

- a. is not possible because $n=0$ is wrong.
 b. is possible.
 c. is not possible because $l=n$ is wrong.
 d. is not possible because $m=+1$ is wrong.
 e. is not possible.
 f. is not possible because $l=2$ is wrong.
 g. is possible.

EXAMPLE 4.3

What are the speed and de Broglie wavelength of an electron that has been accelerated by a potential difference of 500 V?

Sol. The KE of the electron under a PD of 500 V is

$$\frac{1}{2}mv^2 = eV$$

$$v = \left(\frac{2eV}{m} \right)^{1/2}$$

$$= \left(\frac{2 \times (1.602 \times 10^{-19} \text{ C}) (500 \text{ V})}{9.1 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

$$= 1.326 \times 10^7 \text{ m s}^{-1}$$

Using de Broglie equation,

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.26 \times 10^{-34} \text{ J s}}{(9.1 \times 10^{-31} \text{ kg}) (1.326 \times 10^7 \text{ m s}^{-1})} = 5.5 \times 10^{-11} \text{ m}$$

EXAMPLE 4.4

Calculate the IE of (a) one Li^{2+} ion (b) one mole of Li^{2+} ions. Given Rydberg constant = $1.0974 \times 10^7 \text{ m}^{-1}$.

Sol. For ionisation, $n_1 = 1$, $n_2 = \infty$

\therefore IE is given by

$$\text{a. } \Delta E = Z^2 R h c = (9) (1.974 \times 10^7 \text{ m}^{-1}) \times (6.26 \times 10^{-34} \text{ J s}) (3 \times 10^8 \text{ m s}^{-1})$$

$$= 19.638 \times 10^{-18} \text{ J}$$

$$\text{b. } \Delta E = N_A \Delta E = (6.023 \times 10^{23} \text{ mol}^{-1}) (19.638 \times 10^{-18} \text{ J})$$

$$= 1.118 \times 10^7 \text{ J mol}^{-1}$$

$$= 1.118 \times 10^4 \text{ kJ mol}^{-1}$$

EXAMPLE 4.5

In an oil drop experiment, the following charges (in arbitrary units) were found on a series of oil droplets: 2.30×10^{-15} , 6.90×10^{-15} , 1.38×10^{-14} , 5.75×10^{-15} , 3.45×10^{-15} , 1.96×10^{-14} . Calculate the magnitude of the charge on the electron.

Sol. 1.15×10^{-15} is the largest number that divides all the listed charges evenly. The smallest of the charges listed is 2.30×10^{-15} , but this charge does not divide into all the others an even number of times; hence, 2.30×10^{-15} must represent the charge of two electrons.

EXAMPLE 4.6

The wave number of the first line in the Balmer series of hydrogen is 15200 cm^{-1} . What is the wave number of the first line in the Balmer series of Be^{3+} ?

Sol. $\Delta E(\text{Be}) = Z^2 \Delta E(\text{H})$

$$\bar{\nu}(\text{Be}) = 16 \bar{\nu}(\text{H})$$

$$= 16 (15200 \text{ cm}^{-1}) = 2.43 \times 10^5 \text{ cm}^{-1}$$

EXAMPLE 4.7

- What optical transition in the He^{\oplus} spectrum would have the same λ as the first Lyman transition of hydrogen ($n = 2$ to $n = 1$)?
- What is the IP of He^{\oplus} ?
- What is the radius of the first Bohr orbit for He^{\oplus} ?

Sol.

$$\text{a. } \bar{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The first Lyman transition for hydrogen is

$$\bar{\nu} = R \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \quad \dots(\text{i})$$

$$\text{For He}^{\oplus}, \bar{\nu} = R(2)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots(\text{ii})$$

The Z^2 term can just be compensated by increasing n_1 and n_2 by a factor of 2 each. The transition in question is thus the transition from $n = 4$ to $n = 2$.

- The second IP of He is the same as the IP of He^{\oplus} and the Bohr equation may be applied to the ground state of He^{\oplus} , for which $n = 2$ and $n = 1$.

$$\text{IP}(\text{He}^{\oplus}) = Z^2 \times \text{IP}(\text{H}) = 4 \times 13.6 \text{ eV} = 54.4 \text{ eV}$$

$$\text{c. } r = \frac{n^2 a_0}{Z} = \frac{0.529 \text{ \AA}}{2} = 0.264 \text{ \AA}$$

EXAMPLE 4.8

Calculate the velocity of an electron placed in third orbit of H atom. Also calculate the number of revolution per second round the nucleus.

Sol. For CGS system $v_n = \sqrt{\left(\frac{Ze^2}{mr_n} \right)}$

For electron, $e = 4.803 \times 10^{-10} \text{ esu}$

$$m = 9.108 \times 10^{-28} \text{ g}$$

$$\text{Radius of third orbit} = r_1 \times n^2 = 0.529 \times 10^{-8} \times 9 \text{ cm}$$

$$\therefore v_n = \sqrt{\frac{1 \times (4.803 \times 10^{-10})^2}{9.108 \times 10^{-28} \times 0.529 \times 10^{-8} \times 9}}$$

$$= 7.29 \times 10^7 \text{ cm s}^{-1}$$

Now circumference of third orbit

$$= 2 \times \pi \times 0.529 \times 10^{-8} \times 9$$

$$= 29.93 \times 10^{-8} \text{ cm}$$

Therefore, number of revolution per second

$$= \frac{v_n}{2\pi r} = \frac{7.29 \times 10^7}{29.93 \times 10^{-8}} = 2.43 \times 10^{14}$$

EXAMPLE 4.9

The velocity of an electron in a certain Bohr orbit of H atom bears the ratio 1:275 to the velocity of light.

- What is the quantum number (n) of the orbit?
- Calculate the wavenumber of radiations emitted when the electron jumps from $n + l$ state to ground state.

Sol. Velocity of electrons

$$= \frac{1}{275} \times \text{velocity of light}$$

$$= \frac{1}{275} \times 3 \times 10^{10} = 1.09 \times 10^8 \text{ cm s}^{-1}$$

$$\text{Since } v_n = \frac{2\pi e^2}{nh}$$

$$\therefore 1.09 \times 10^8 = \frac{2 \times 3.14 \times (4.803 \times 10^{-10})^2}{6.625 \times 10^{-27} \times n}$$

$$\therefore n = 20.06 \times 10^{-1} = 2 \quad (\text{an integer value})$$

Also when the electron jumps from $n = 3$, i.e., third to ground state

$$v = \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{3^2} \right]$$

$$= 109678 \left[\frac{1}{1} - \frac{1}{9} \right] = 9.75 \times 10^4 \text{ cm}^{-1}$$

EXAMPLE 4.10

The ionisation energy of H atom is 13.6 eV. What will be the ionisation energy of He^{\oplus} and Li^{2+} ions?

Sol. E_1 for $\text{He}^{\oplus} = E_1$ for $\text{H} \times Z^2$

$$= 13.6 \times 4 = 54.4 \text{ eV}$$

E_1 for $\text{Li}^{2+} = E_1$ for $\text{H} \times Z^2$

$$= 13.6 \times 9 = 122.4 \text{ eV}$$

EXAMPLE 4.11

The ionisation energy of He^{\oplus} is $19.6 \times 10^{-18} \text{ J atom}^{-1}$. Calculate the energy of the first stationary state of Li^{2+} .

Sol. E_1 for $\text{Li}^{2+} = E_1$ for $\text{H} \times Z^2 = E_1$ for $\text{H} \times 9$

E_1 for $\text{He}^{\oplus} = E_1$ for $\text{H} \times Z^2 = E_1$ for $\text{H} \times 4$

$$\therefore E_1 \text{ for } \text{Li}^{2+} = E_1 \text{ for } \text{He}^{\oplus} \times \frac{9}{4}$$

$$= 19.6 \times 10^{-18} \times \frac{9}{4}$$

$$= 44.1 \times 10^{-18} \text{ J atom}^{-1}$$

EXAMPLE 4.12

Calculate the shortest and the longest wavelength in H spectrum of the Lyman series. $R_H = 109678 \text{ cm}^{-1}$.

Sol. For Lyman series, $n_1 = 1$

For shortest λ of Lyman series, energy difference in two levels showing transition should be maximum, i.e., $n_2 = \infty$.

$$\therefore \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = 109678$$

$$\therefore \lambda = 911.7 \times 10^{-8} \text{ cm} = 911.7 \text{ Å}$$

For longest λ of Lyman series, energy difference in two levels showing transition should be minimum, i.e., $n_2 = 2$

$$\therefore \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = 109678 \times \frac{3}{4}$$

$$\therefore \lambda = 1215.67 \times 10^{-8} \text{ cm} = 1215.67 \text{ Å}$$

EXAMPLE 4.13

The λ of H_α line of the Balmer series is 6500 Å. What is the λ of H_β line of the Balmer series.

Sol. For H_α line of the Balmer series, $n_1 = 2, n_2 = 3$.

For H_β line of the Balmer series, $n_1 = 2, n_2 = 4$.

$$\therefore \frac{1}{\lambda_{\text{H}_\alpha}} = R_H \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \quad \dots(i)$$

$$\text{and } \frac{1}{\lambda_{\text{H}_\beta}} = R_H \left[\frac{1}{2^2} - \frac{1}{4^2} \right] \quad \dots(ii)$$

By equations (i) and (ii), we get

$$\therefore \frac{\lambda_\beta}{\lambda_\alpha} = \frac{\frac{1}{4} - \frac{1}{16}}{\frac{1}{4} - \frac{1}{9}}$$

$$\therefore \lambda_\beta = \lambda_\alpha \times \left[\frac{80}{108} \right] = 6500 \times \frac{80}{108} = 4814.8 \text{ Å}$$

EXAMPLE 4.14

Calculate λ of the radiations when an electron jumps from third to the second orbit for H atom. The electronic energy in second and third Bohr orbits of the atom are -5.42×10^{-12} and -2.41×10^{-12} erg, respectively.

Sol. E_3 for H = -2.41×10^{-12} erg

E_2 for H = -5.42×10^{-12} erg

\therefore For a jump from third to second shell,

$$\Delta E = E_3 - E_2 = \frac{hc}{\lambda}$$

$$\therefore \lambda = \frac{hc}{E_3 - E_2}$$

$$= \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{-2.41 \times 10^{-12} + 5.42 \times 10^{-12}}$$

$$= 6502.9 \times 10^{-8} \text{ cm} = 6603 \text{ Å}$$

EXAMPLE 4.15

For He^{\oplus} and Li^{2+} , the energies are related to the quantum number n through an expression

$$E_n = -\frac{Z^2 B}{n^2}, \text{ where } Z \text{ is the atomic number of species and}$$

$$B = 2.179 \times 10^{-18} \text{ J.}$$

a. What is the energy of the lowest level of a He^{\oplus} ion?

b. What is the energy of the third level of Li^{2+} ion?

Sol.

$$\text{a. } E_1 \text{ for } \text{He}^{\oplus} = -\frac{2^2 \times 2.179 \times 10^{-18}}{1^2}$$

$$= -8.716 \times 10^{-18} \text{ J}$$

$$\text{b. } E_3 \text{ for } \text{Li}^{2+} = -\frac{3^2 \times 2.179 \times 10^{-18}}{3^2}$$

$$= -2.179 \times 10^{-18} \text{ J}$$

EXAMPLE 4.16

Calculate the wavelength emitted during the transition of electron in between two levels of Li^{2+} ion whose sum is 4 and difference is 2.

Sol. Let the transition occur in between levels n_1 and n_2 . Thus, if $n_2 > n_1$, then given

$$n_1 + n_2 = 4$$

$$n_2 - n_1 = 2$$

$$\therefore n_1 = 1 \text{ and } n_2 = 3$$

$$\therefore \frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{1^2} - \frac{1}{3^2} \right] \quad (\because Z = 3 \text{ for Li})$$

$$= 109,678 \times 3^2 \times \left[\frac{8}{9} \right]$$

$$\therefore \lambda = 1.13 \times 10^{-6} \text{ cm}$$

EXAMPLE 4.17

The angular momentum of an electron in a Bohr orbit of H atom is $4.2178 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$. Calculate the λ of the spectral line emitted when the electron falls from this level to the next lower level.

Sol. Given $mvr = \frac{nh}{2\pi}$

$$\therefore \frac{nh}{2\pi} = 4.2178 \times 10^{-34}$$

$$\text{or } n = \frac{4.2178 \times 10^{-34} \times 2 \times 3.14}{6.625 \times 10^{-34}} = 4$$

$$\text{Thus } \frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The transition spectral line for fourth to third shell is

$$\frac{1}{\lambda} = 109678 \left[\frac{1}{3^2} - \frac{1}{4^2} \right]$$

$$\therefore \lambda = 1.8 \times 10^{-4} \text{ cm}$$

EXAMPLE 4.18

A certain laser transition emits 6.37×10^{15} quanta per second per square metre. Calculate the power out put in joule per square metre per second. Given $\lambda = 632.8 \text{ nm}$.

Sol. Energy falling per square metre per second is

Number of quanta falling per square metre per second
 \times Energy of one quantum

$$= 6.37 \times 10^{15} \times \frac{hc}{\lambda}$$

$$= 6.37 \times 10^{15} \times \frac{6.25 \times 10^{-34} \times 3 \times 10^8}{632.8 \times 10^{-9}}$$

$$= 2 \times 10^{-3} \text{ J m}^{-2} \text{ s}^{-1}$$

EXAMPLE 4.19

A base ball of mass 200 g is moving with velocity of $3 \times 10^3 \text{ cm s}^{-1}$. If we can locate the base ball with an error equal to the magnitude of the wavelength of the light used (5000 \AA), how will the uncertainty in momentum be compared with the total momentum of the base ball?

Sol. Momentum of the base ball = mv

$$p = 200 \times 3 \times 10^3 = 6 \times 10^5 \text{ cm g s}^{-1}$$

$$\Delta p \Delta x \geq h/4\pi$$

$$\Delta p \geq \frac{h}{4\pi \Delta x} \quad (\Delta x = 5000 \times 10^{-8} = 5 \times 10^{-5})$$

$$\geq \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 5 \times 10^{-5}}$$

$$\frac{\Delta p}{p} \geq \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 5 \times 10^{-5} \times 6 \times 10^5}$$

$$= 1.758 \times 10^{-29}$$

EXAMPLE 4.20

The critical wavelength for producing photoelectric effect in a metal is 2500 \AA . What wavelength would be necessary to produce photoelectric effect from this metal, having twice the KE of those produced at 2000 \AA .

Sol. $\text{KE}_{2000} = h\nu_{2000} - h\nu_0 = hc \left(\frac{1}{\lambda_{2000}} - \frac{1}{\lambda_0} \right)$

$$\text{KE}_{\text{new}} = h\nu_{\text{new}} - h\nu_0 = hc \left(\frac{1}{\lambda_{\text{new}}} - \frac{1}{\lambda_0} \right)$$

$$\text{KE}_{\text{new}} = 2 \times \text{KE}_{2000}$$

$$2 = \frac{hc \left(\frac{1}{\lambda_{\text{new}}} - \frac{1}{2500} \right)}{hc \left(\frac{1}{2000} - \frac{1}{2500} \right)}; \lambda = 1666.66 \text{ \AA}$$

Level-II**EXAMPLE 4.21**

A photon of frequency ν causes photoelectric emission from a surface with threshold frequency ν_0 . The de Broglie wavelength (λ) of the photo-electron emitted is given by

a. $\Delta n = \frac{h}{2m\lambda}$

b. $\Delta n = \frac{h}{\lambda}$

c. $\left[\frac{1}{\nu_0} - \frac{1}{\nu} \right] = \frac{mc^2}{n}$

d. $\lambda = \sqrt{\frac{h}{2m \Delta \nu}}$

Sol.

d. According to the photoelectric equation,

$$E_i = \text{IE} + \text{KE}$$

$$\text{or } E_i = \text{Threshold energy or work function} + \text{KE}$$

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$\Rightarrow \frac{1}{2}mv^2 = h(\nu - \nu_0) = h \Delta \nu$$

We know that

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

$$\therefore v = \frac{h}{m\lambda}$$

Substituting this value in equation (i), we get

$$\frac{1}{2}m \frac{h^2}{m^2 \lambda^2} = h \Delta \nu$$

$$\frac{h}{2m\lambda^2} = \Delta \nu$$

$$\therefore \lambda = \sqrt{\frac{h}{2m \Delta \nu}}$$

Hence the answer is (d)

EXAMPLE 4.22

O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom 1.967 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen requires 498 kJ mol^{-1} . What is the maximum wavelength effective for photochemical dissociation of O_2 ?

Sol. We know



Energy required for simple dissociation of O_2 into two

$$\text{normal atoms} = \frac{498 \times 10^3}{6.023 \times 10^{23}} \text{ J mol}^{-1}$$

If one atom in excited state has more energy, i.e., 1.967 eV = $1.967 \times 1.602 \times 10^{-19} \text{ J}$, the energy required for photochemical dissociation of O_2 is

$$= \frac{498 \times 10^3}{6.023 \times 10^{23}} + 1.967 \times 1.602 \times 10^{-19}$$

$$= 82.68 \times 10^{-20} + 31.51 \times 10^{-20}$$

$$= 114.19 \times 10^{-20} \text{ J}$$

$$E = \frac{hc}{\lambda}$$

$$114.19 \times 10^{-20} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\lambda = 1740.2 \times 10^{-10} \text{ m} = 1740.2 \text{ \AA}$$

EXAMPLE 4.23

A stationary He^+ ion emits a photon corresponding to the first line (H_α) of the Lyman series. The photon thus emitted strikes a H atom in the ground state. Find the velocity of the photoelectron ejected out of the hydrogen atom. The value of R is $1.097 \times 10^7 \text{ m}^{-1}$

Sol. The difference in energy (ΔE) will be equal to the energy of the photon emitted.

The first line in Lyman series corresponds to the transition $2 \rightarrow 1$.

$$\Delta E = 2.18 \times 10^{-18} (2)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \text{ J per atom}$$

$$= 6.54 \times 10^{-18} \text{ J}$$

A photon carrying this energy strikes a H atom in the ground state. Note that the ionisation energy of H atom is $+2.18 \times 10^{-18} \text{ J}$. This will be the work function of H atom. Using the Einstein's photoelectric equation

$$\text{KE} = E_i - W_0 = \frac{1}{2} m_e v_e^2$$

[E_i = Incident energy]

$$\Rightarrow v_e = \sqrt{\frac{2(E_i - W_0)}{m_e}}$$

$$= \sqrt{\frac{2(6.54 \times 10^{-18} - 2.18 \times 10^{-18})}{9.1 \times 10^{-31}}}$$

$$= 3.09 \times 10^6 \text{ m s}^{-1}$$

We can also calculate the wavelength of electron ejected out to be $2.36 \times 10^{-10} \text{ m} = 2.36 \text{ \AA}$

$$\lambda_e = \frac{h}{m_e v_e} = \frac{6.626 \times 10^{-34}}{9.7 \times 10^{-38} \times 3.09 \times 10^6 \text{ m}} = 2.36 \text{ \AA}$$

EXAMPLE 4.24

When photons of energy 25 eV strike the surface of a metal A, the ejected photoelectrons have the maximum kinetic energy T_A eV and de Broglie wavelength λ_A . The maximum kinetic energy of photoelectrons liberated from another metal B by photons of energy 4.70 eV is $T_B = (T_A - 1.50) \text{ eV}$. If the de Broglie wavelength of these photoelectrons is $\lambda_B = 2\lambda_A$, then

I. $(W_0)_A = 2.25 \text{ eV}$

II. $(W_0)_B = 4.2 \text{ eV}$

III. $T_A = 2.0 \text{ eV}$

IV. $T_B = 3.5 \text{ eV}$

The correct option is

a. I, II

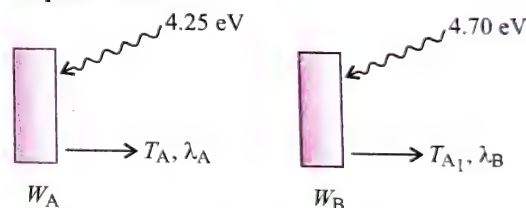
b. II, III, IV

c. I, II, III

d. I, II, III, IV

Sol. c. I, II, II

Explanation:



$$W_A + T_A = 4.25 \Rightarrow W_A = 2.25 \text{ eV}$$

$$W_A + T_B = 4.7 \Rightarrow W_B = 4.2 \text{ eV}$$

$$\lambda_B = 2\lambda_A$$

$$\Rightarrow \text{KE}_A = 4\text{KE}_B$$

$$\Rightarrow T_A = 4(T_B)$$

$$\Rightarrow T_A = 2.0 \text{ eV}$$

$$T_B = 0.5 \text{ eV}$$

Hence, option (c).

EXAMPLE 4.25

In hydrogen atom an orbit has a diameter of about 16.92 Å. What is the maximum number of electrons that can be accommodated?

a. 8

b. 32

c. 50

d. 72

Sol. b. Diameter of hydrogen atom = 16.92 Å

$$\text{Radius of an atom} = \frac{16.92}{2} = 8.46 \text{ \AA}$$

We know:

$$r_n = \frac{0.53n^2}{Z} \text{ \AA}$$

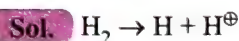
$$8.46 = \frac{0.53n^2}{1}$$

$$\text{or } n = 4$$

Therefore, the maximum number of electrons in the fourth orbit are = $2n^2 = 2 \times (4)^2 = 32$

EXAMPLE 4.26

Hydrogen, when subjected to photo-dissociation, yields one normal atom and one atom possessing 1.97 eV more energy than normal atom. The bond dissociation energy of hydrogen molecule into normal atoms is 103 kcal mol⁻¹. Compute the wavelength of effective photon for photo-dissociation of hydrogen molecule in the given case.



where H is normal H atom and H[⊕] is excited H atom. So the energy required to dissociate H₂ in this manner will be greater than the usual bond energy of H₂ molecule.

$E_{(\text{absorbed})}$ = dissociation energy of H₂ + extra energy of excited atom

$$\begin{aligned} \text{Energy required to dissociate in normal manner} &= 103 \times 10^3 \text{ cal} \quad (\text{given}) \\ &= \frac{103 \times 10^3 \times (4.18)}{6 \times 10^{23}} \\ &= 7.716 \times 10^{-19} \text{ J atom}^{-1} \end{aligned}$$

The extra energy possessed by the excited atom is

$$1.97 \text{ eV} = 1.97 \times 1.6 \times 10^{-19} \text{ J} = 3.152 \times 10^{-19}$$

$$\begin{aligned} E_{(\text{absorbed})} &= 7.716 \times 10^{-19} + 3.152 \times 10^{-19} \\ &= 1.0868 \times 10^{-18} \text{ J} \end{aligned}$$

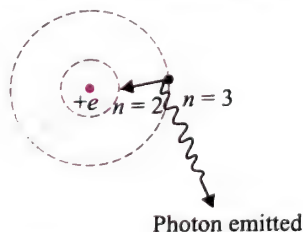
Now calculate the wavelength of photon corresponding to this energy.

$$\begin{aligned} \lambda &= \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{1.0868 \times 10^{-18}} \\ &= 1.830 \times 10^{-7} \text{ m} = 1830 \text{ \AA} \end{aligned}$$

EXAMPLE 4.27

Calculate the wavelength and wave-number of the spectral line when an electron of H atom falls from a higher energy state $n = 3$ to a state $n = 2$. Also determine the energy of a photon to ionise this atom by removing the electron from the second orbit. Compare it with the energy of photon required to ionise the atom by removing the electron from the ground state.

Sol.

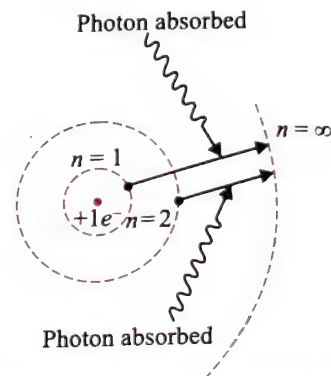


First calculate the energy difference (ΔE) between the orbits $n = 3$ and $n = 2$ using

$$\begin{aligned} \Delta E &= 2.18 \times 10^{-18} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ J} \\ \Delta E_{(3 \rightarrow 2)} &= 2.18 \times 10^{-18} (1)^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \text{ J} \quad (Z = 1) \\ &= 3.03 \times 10^{-19} \text{ J} \end{aligned}$$

Now this energy difference is the energy of the photon emitted.

$$\begin{aligned} E_{\text{Photon}} &= h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \\ \Rightarrow \frac{hc}{\lambda} &= 3.03 \times 10^{-19} \Rightarrow \lambda = 6560.3 \text{ \AA} \\ \text{and } \bar{\nu} &= \frac{1}{\lambda} = 1.52 \times 10^{-6} \text{ m}^{-1} \end{aligned}$$



To ionise the atom from $n = 2$, the transition will be $n = 2 \rightarrow n = \infty$

$$\begin{aligned} \Delta E_{(2 \rightarrow \infty)} &= 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) \text{ J} \\ &= 5.45 \times 10^{-19} \text{ J} \end{aligned}$$

To ionise the atom from the ground state ($n = 1$), the transition is $1 \rightarrow \infty$.

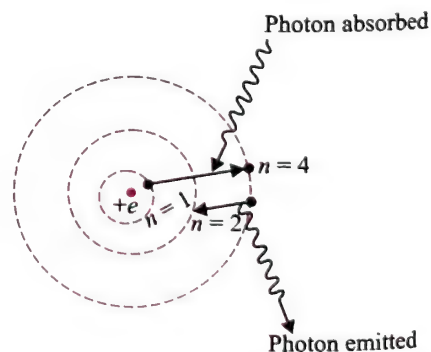
$$\begin{aligned} \Delta E &= 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) \\ &= 2.18 \times 10^{-18} \text{ J} \end{aligned}$$

EXAMPLE 4.28

A hydrogen atom in the ground state is hit by a photon exciting the electron to the third excited state. The electron then drops to the second orbit. What is the frequency of radiation emitted and absorbed in the process?

Sol. Energy is absorbed when the electron moves from the ground state ($n = 1$) to the third excited state ($n = 4$).

First calculate the energy difference between $n = 1$ and $n = 4$.



$$\text{Use } \Delta E_{(1 \rightarrow 4)} = 2.18 \times 10^{-18} \times Z^2 \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Here $Z = 1$, $n_1 = 1$, $n_2 = 4$

$$\Delta E_{(1 \rightarrow 4)} = 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{4^2} \right) \text{ J}$$

$$= 2.04 \times 10^{-18} \text{ J}$$

This is the energy of the photon absorbed.

$$E_{\text{photon}} = h\nu = 2.04 \times 10^{-18} \text{ J to get}$$

$$\Rightarrow \nu = 3.08 \times 10^{15} \text{ Hz}$$

Similarly, when electron jumps from $n = 4$ to $n = 2$, the energy is emitted and is given by the same relation.

Putting $n_1 = 2$ and $n_2 = 4$ in the expression of ΔE , we get

$$\Delta E_{(4 \rightarrow 2)} = 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \text{ J}$$

$$= 4.08 \times 10^{-19} \text{ J}$$

This is the energy of the photon emitted.

$$E_{\text{photon}} = h\nu = 4.08 \times 10^{-19} \text{ J}$$

$$\Rightarrow \nu = 6.16 \times 10^{14} \text{ Hz}$$

EXAMPLE 4.29

An electron in the first excited state of H atom absorbs a photon and is further excited. The de Broglie wavelength of the electron in this state is found to be 13.4 \AA . Find the wavelength of the photon absorbed by the electron in angstrom. Also find the longest and the shortest wavelength emitted when this electron de-excites back to the ground state.

Sol.

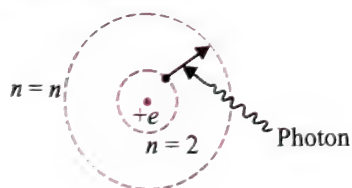
Note: The energy state $n = 1$ is known as the ground state.

The energy state $n = 2$ is known as the first excited state.

The energy state $n = 3$ is known as the second excited state and so on.

The electron from $n = 2$ absorbs a photon and is further excited to a higher energy level (say n).

The electron in this energy level (n) has a de Broglie wavelength (λ) = 13.4 \AA .



$$v_e = \frac{h}{m_e \lambda_e}$$

$$\text{and } v_e = 2.18 \times 10^6 \frac{Z}{n} \text{ m s}^{-1}$$

[v_e is the velocity of the electron in n th orbit]

$$\Rightarrow v_e = \frac{h}{\lambda m} = 2.18 \times 10^6 \left(\frac{1}{n} \right)$$

$$\Rightarrow \frac{6.626 \times 10^{-34}}{(13.4 \times 10^{-10}) \times (9.1 \times 10^{-31})} = 2.18 \times 10^6 \times \frac{1}{n}$$

$$\Rightarrow n = 4$$

Now find the wavelength of the photon responsible for the excitation from $n = 2$ to $n = 4$.

Using the relation

$$\Delta E_{(2 \rightarrow 4)} = 2.18 \times 10^{-18} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= 4.09 \times 10^{-19} \text{ J} \quad [n_1 = 2, n_2 = 4, Z = 1]$$

$$\Rightarrow \frac{hc}{\lambda} = 4.09 \times 10^{-19}$$

$$\Rightarrow \lambda = 4863.1 \text{ \AA}$$

The longest wavelength emitted when this electron (from $n = 4$) falls back to the ground state will correspond to the minimum energy transition.

The transition corresponding to the minimum energy will be $4 \rightarrow 3$.

The transition corresponding to the maximum energy will be $4 \rightarrow 1$.

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = h\nu$$

$$\Rightarrow \Delta E \propto \frac{1}{\lambda_{\text{photon}}} \text{ or } \Delta E \propto \nu_{\text{photon}}$$

Using the same relation

$$\Delta E_{(4 \rightarrow 3)} = 2.18 \times 10^{-18} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$[n_1 = 3, n_2 = 4, Z = 1]$$

$$\Rightarrow \Delta E_{(4 \rightarrow 3)} = 1.06 \times 10^{-19} \text{ J}$$

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = 1.06 \times 10^{-19} \text{ J}$$

$$\Rightarrow \lambda = 18752.8 \text{ \AA}$$

Shortest wavelength : $4 \rightarrow 1$

$$\Delta E_{(4 \rightarrow 1)} = 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{4^2} \right)$$

$$= 2.04 \times 10^{-18} \text{ J}$$

$$\Rightarrow \Delta E_{(4 \rightarrow 1)} = E_{\text{photon}} = \frac{hc}{\lambda}$$

$$\Rightarrow \lambda = 973.2 \text{ \AA}$$

EXAMPLE 4.30

A single electron orbits around a stationary nucleus of charge $+Ze$, where Z is a constant and e is the magnitude of electronic charge. It requires 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit.

a. Find the value of Z .

b. Find the energy required to excite the electron from $n = 3$ to $n = 4$.

c. Find the wavelength of radiation to remove the electron from the second Bohr orbit to infinity.

d. Find the kinetic energy, potential energy, and angular momentum of the electron in the first orbit.

e. Find the ionisation energy of above electron system in electronvolt.

Sol. Since the nucleus has a charge $+Ze$, the atomic number of the ion is Z .

a. The transition is $n_1 = 2 \rightarrow n_2 = 3$ by absorbing a photon of energy 47.2 eV .

$$\Rightarrow \Delta E = 47.2 \text{ eV}$$

Using the relation:

$$\Delta E = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV}$$

$$\Rightarrow 47.2 = 13.6Z^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \Rightarrow Z = 5$$

- b. The required transition is $n_1 = 3 \rightarrow n_2 = 4$ by absorbing a photon of energy ΔE .

Find ΔE by using the relation.

$$\Delta E = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \Delta E = 13.6(5)^2 \left(\frac{1}{3^2} - \frac{1}{4^2} \right)$$

$$\Rightarrow \Delta E = 16.53 \text{ eV}$$

- c. The required transition is $n_1 = 2 \rightarrow n_2 = \infty$ by absorbing a photon of energy ΔE .

Find ΔE by using the relation.

$$\Delta E = 13.6(5)^2 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right)$$

$$\Rightarrow \Delta E = 85 \text{ eV}$$

Find λ of radiation corresponding to energy 85 eV.

$$\Rightarrow \lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{85(1.6 \times 10^{-19})}$$

$$= 146.25 \times 10^{-10} = 146.25 \text{ Å}$$

- d. If energy of electron be E_n , then $\text{KE} = -E_n$ and $\text{PE} = 2E_n$.

$$E_n = \frac{-13.6Z^2}{n^2} = \frac{-13.6 \times 5^2}{1^2} = -340 \text{ eV}$$

$$\text{KE} = (-340 \text{ eV}) = 340 \text{ eV}$$

$$\text{PE} = 2(-340 \text{ eV}) = -680 \text{ eV}$$

- e. Ionization energy $= \Delta E = 13.6(5)^2 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right)$

$$\therefore \Delta E = 85 \text{ eV}$$

EXAMPLE 4.32

One mole of He^{\oplus} ions is excited. An analysis showed that 50% of ions are in the third energy level, 25% are in the second energy level, and the remaining are in the first energy level. Calculate the energy emitted in kilojoules when all the ions return to the ground state.

Sol. 50% in $n = 3 \xrightarrow{E_1} 1$
25% in $n = 2 \xrightarrow{E_2} 1$

$$\Delta E = 2.176 \times 10^{-18} Z^2 \left[\frac{1}{1^2} - \frac{1}{n^2} \right] \text{ J per atom}$$

Energy released when electron falls to $n = 1$ is

$$= \left\{ 50\% \left[2.176 \times 10^{-18} \times 4 \left(1 - \frac{1}{9} \right) \right] + 25\% \left[2.176 \times 10^{-18} \times 4 \left(1 - \frac{1}{4} \right) \right] \right\}$$

$$\times 6 \times 10^{23} \times 10^{-3} (\text{kJ mol}^{-1})$$

EXAMPLE 4.33

The kinetic energy of an electron in H like atom is 6.04 eV. Find the area of the third Bohr orbit to which this electron belongs. Also report the atom.

Sol. $\text{KE} = 6.04$ in third orbit

$$E_{\text{total}} = \text{KE} + \text{PE} = \text{KE} - 2 \times \text{KE}$$

$$\Rightarrow -\text{KE} = -6.04 \text{ eV}$$

E_1 for H = -13.6 eV and not for any orbit $E = -6.04$ eV for H atom. Thus, atom for which KE is given is other than H.

$$E_n \text{ of H-like atom} = E_{\text{H}} \times Z^2$$

$$\frac{E_1}{n^2} \times Z^2 \Rightarrow 6.04 = \frac{13.6}{3^2} \times Z^2$$

$$Z^2 = 3.99 \approx 4 \Rightarrow Z = 2$$

Hence, the atom is He^{\oplus} . So

$$\Rightarrow r_n = 0.529 \times \frac{n^2}{Z} = 0.529 \times \frac{3^2}{2} = 2.3805 \text{ Å}$$

$$\text{Area, } \pi r^2 = \frac{22}{7} \times (2.3805 \times 10^{-8})^2$$

$$= 17.8 \times 10^{-16} \text{ cm}^2$$

EXAMPLE 4.34

Determine the frequency of revolution of an electron in the second Bohr orbit in hydrogen atom.

Sol. The frequency of revolution of an electron is given by

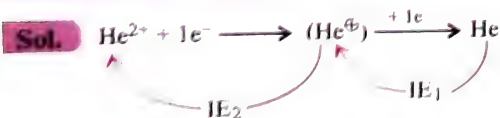
$$\text{Frequency} = \frac{1}{\text{Time period}}$$

$$\text{Time period} = \frac{\text{Total distance covered in one revolution}}{\text{Velocity}}$$

$$= \frac{2\pi r}{v}$$

EXAMPLE 4.31

Find the energy released (in joules) when a doubly ionised helium ion (He^{2+}) takes up two electrons to form a helium atom in the ground state. The first ionisation energy of a helium atom is $3.4 \times 10^{-19} \text{ J}$.



IE = ionisation energy of He

$$\text{IE}_1 = 3.4 \times 10^{-19} \text{ J}$$

$$\text{IE}_2 = \text{IE of He}^{\oplus} \text{ ion} = 2.17 \times 10^{-18} \times (4) = 8.68 \times 10^{-18} \text{ J}$$

Total energy released

$$\text{IE}_1 + \text{IE}_2 = (3.4 \times 10^{-19} + 8.68 \times 10^{-18}) \text{ J}$$

$$= 90.2 \times 10^{-19} = 9.02 \times 10^{-18} \text{ J}$$



$$\therefore \text{Frequency} = \frac{v}{2\pi r}$$

Calculate the velocity (v_2) and radius (r_2) of the electron in the second Bohr orbit in H atom

$Z = 1$ for H atom

$$\text{Using } r_n = 0.529 \frac{n^2}{Z} \text{ \AA}$$

We get,

$$r_2 = 0.529 \times 10^{-10} \frac{(2)^2}{1} \text{ m} = 1.12 \times 10^{-10} \text{ m}$$

$$v_n = 2.18 \times 10^6 (1/n) \text{ m s}^{-1}$$

$$v_2 = 2.18 \times 10^6 (1/2) = 1.09 \times 10^6 \text{ m s}^{-1}$$

$$\therefore \text{Frequency} = \frac{v_2}{2\pi r_2} = \frac{1.09 \times 10^6}{2(\pi)(1.12 \times 10^{-10})}$$

$$v = 8.18 \times 10^{14} \text{ Hz}$$

Note: Frequency of revolution (f) = $\frac{1}{T}$

$$\text{where } T = -\frac{2\pi r}{v} \propto \frac{n^3}{Z^2} \quad \left[\because r \propto \frac{n^2}{Z} \text{ and } v \propto \frac{Z}{n} \right]$$

EXAMPLE 4.35

Give the names of seven f -orbitals and how they are represented.

Sol. A complete set of seven f -orbitals is shown in the table and the figure given here.

As with d -orbitals, there is no unique way of representing them, nor is there even a way which is optimum for all problems. The figure presents two sets, a 'General set' and a 'cubic set'. The latter is advantageous in considering the properties of the orbitals in cubic (i.e. octahedral and tetrahedral fields).

Table: Names and shapes of f -orbitals

The general set	The cubic set
1. xz^2	5. z^3 or x^3 or y^3 .
2. $x(x^2 - 3y^2)$	i. x^3 same as z^3 except lies along the x -axis.
3. $y(3y^2 - x^2)$	ii. y^3 same as z^3 except lies along the y -axis
4. $z(x^2 - y^2)$ or xyz	6. xyz
Same as the corresponding orbitals in the cubic set	7. $z(x^2 - y^2)$
	or
	$y(z^2 - x^2)$
	$z(x^2 - y^2)$
	Same as xyz but rotated 45° about the x, y, z axes

The general set

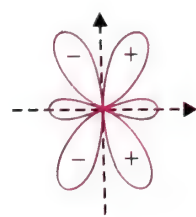
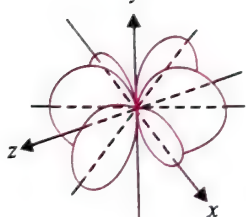
Perspective drawing

Cross-section plot

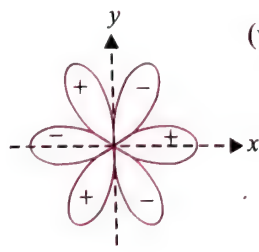
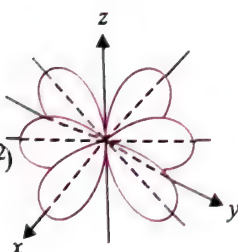


(A section has been cut out of the two 'collars' for clarity)

(i) xz^2



(ii) $x(x^2 - 3y^2)$



(iii) $y(3y^2 - x^2)$ Same as $x(x^2 - 3y^2)$ except lies along the y axis.

(iv) $z(x^2 - y^2)$ } Same as the corresponding orbitals in the cubic set.
 xyz

The cubic set

Perspective drawing

Cross-section plot

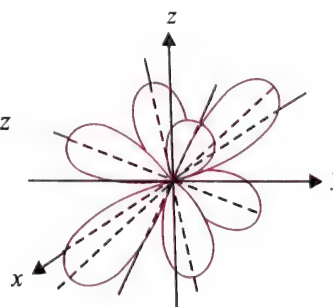


(v) z^3

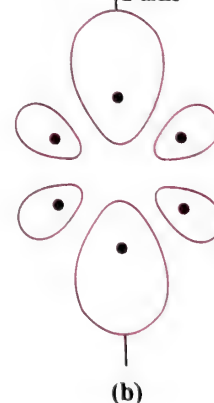
(A section has been cut out of the two 'collars' for clarity)

x^3 Same as z^3 except lies along the x axis
 y^3 Same as z^3 except lies along the y axis

(vi) xyz



Contour plot
 z axis



(b)

$z(x^2 - y^2)$ } Same as the xyz but rotated 45°
 $y(z^2 - x^2)$ } about the x, y and z axes.
 $x(z^2 - y^2)$ }

(a)

Figure: The f -orbitals: (a) Plots of the angular part of the wave functions of the f orbital; (b) contours of a $4f$ orbital. Dots indicate maxima in electron density. The lines are drawn for densities which are 10% of maximum.

Exercises

Single Correct Answer Type

- Atomic mass of an element is not necessarily a whole number because
 - It contains electrons, protons, and neutrons
 - It exists in allotropic forms
 - It contains isotopes
 - Atoms are no longer indivisible
- Which of the following properties of an element is a whole number?
 - Atomic mass
 - Atomic volume
 - Atomic radius
 - Mass number
- Which of the following sets of quantum number is allowable:
 - $n = 2, l = 1, m = 0, s = +1/2$
 - $n = 2, l = 2, m = -1, s = -1/2$
 - $n = 2, l = -2, m = 1, s = +1/2$
 - $n = 2, l = 1, m = 0, s = 0$
- Which shape is associated with the orbital designated by $n = 2; l = 1$?
 - Spherical
 - Tetrahedral
 - Dumb-bell
 - Pyramidal
- An isotone of ${}_{32}\text{Ge}^{76}$ is
 - ${}_{32}\text{Ge}^{77}$
 - ${}_{33}\text{As}^{77}$
 - ${}_{34}\text{Se}^{77}$
 - ${}_{34}\text{Se}^{78}$
 - Only (i) and (ii)
 - Only (ii) and (iii)
 - Only (ii) and (iv)
 - (ii), (iii), and (iv)
- The transition of electrons in H atom that will emit maximum energy is
 - $n_3 \rightarrow n_2$
 - $n_4 \rightarrow n_3$
 - $n_5 \rightarrow n_4$
 - $n_6 \rightarrow n_5$
- The limiting line in Balmer series will have a frequency of
 - $32.29 \times 10^{15} \text{ s}^{-1}$
 - $3.65 \times 10^{14} \text{ s}^{-1}$
 - $-8.22 \times 10^{14} \text{ s}^{-1}$
 - $8.22 \times 10^{14} \text{ s}^{-1}$
- The fundamental particles which are responsible for keeping nucleons together is:
 - Meson
 - Antiproton
 - Positron
 - Electron
- Which of the following is not a characteristic of Planck's quantum theory of radiation?
 - Radiations are associated with energy
 - Magnitude of energy associated with a quantum is equal to $h\nu$.
 - Radiation energy is neither emitted nor absorbed continuously.
 - A body can emit less or more than a 'quantum of energy.

- Which out of the following configurations is incorrect?
 - $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^0$
 - $1s^2 2s^2 2p_x^1 2p_y^1$
 - $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^1$

- Which of the following set of quantum numbers is an impossible arrangement?
 - $n = 3, m = -2, s = +1/2$
 - $n = 4, m = 3, s = +1/2$
 - $n = 5, m = 2, s = -1/2$
 - $n = 3, m = -3, s = -1/2$

- Which of the following statements about quantum numbers is wrong:
 - If the value of $l = 0$, the electron distribution is spherical
 - The shape of the orbital is given by subsidiary quantum number.
 - The Zeeman's effect is explained by magnetic quantum number.
 - The spin quantum number gives the orientations of electron cloud.

- Bohr's model of atom is not in agreement with
 - Line spectra hydrogen atom
 - Pauli's principle
 - Planck's theory
 - Heisenberg's principle

- If the energy of electron in H atom is given by expression $-1312/n^2 \text{ kJ mol}^{-1}$, then the energy required to excite the electron from ground state to second orbit is
 - 328 kJ
 - 656 kJ
 - 984 kJ
 - 1312 kJ

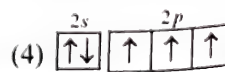
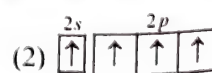
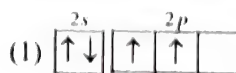
- Which experimental observation given in the first column correctly accounts for the phenomenon given in the second column?

Experimental observation

Phenomenon

- | | |
|-----------------------------------|-----------------------------|
| (1) X-ray spectra | p. Charge on nucleus |
| (2) α -particle scattering | q. Quantised electron orbit |
| (3) Photo electric effect | r. The nuclear atom |
| (4) Emission spectra | s. Quantisation of energy |

- For which of the following electron distributions in ground state, the Pauli's exclusion principle is violated?



- Which of the following orbital does not make sense?

- 3d
- 2f
- 5p
- 7s

18. Which of the following sets of quantum numbers is not possible?

- (1) $n=4, l=1, m=0, s=+1/2$
 (2) $n=4, l=3, m=-3, s=-1/2$
 (3) $n=4, l=-1, m=+2, s=-1/2$
 (4) $n=4, l=1, m=0, s=-1/2$

19. The possible sub-shells in $n=3$ energy shell are:

- (1) s, p, d (2) s, p, d, f (3) s, p (4) s only

20. In the Schrödinger's wave equation ψ represents

- (1) Orbit (2) Wave function
 (3) Wave (4) Radial probability

21. Heisenberg's uncertainty principle rules out the exact simultaneous measurement of:

- (1) Probability and intensity
 (2) Energy and velocity
 (3) Charge density and radius
 (4) Position and velocity

22. The two electrons have the following sets of quantum numbers:

X: 3, 2, -2, +1/2

Y: 3, 0, 0, +1/2

What is true of the following

- (1) X and Y have same energy.
 (2) X and Y have unequal energy.
 (3) X and Y represent same electron.
 (4) None of the statement is correct.

23. When electronic transition occurs from higher energy state to lower energy state with energy difference equal to ΔE electron volts, the wavelength of the line emitted is approximately equal to

- (1) $\frac{12395}{\Delta E} \times 10^{-10} \text{ m}$ (2) $\frac{12395}{\Delta E} \times 10^{10} \text{ m}$
 (3) $\frac{12395}{\Delta E} \times 10^{-10} \text{ cm}$ (4) $\frac{12395}{\Delta E} \times 10^{10} \text{ cm}$

24. Which of the following statements concerning Bohr's model is false?

- (1) It predicts that probability of electron near nucleus is more.
 (2) The angular momentum of electron in H atom = $nh/2\pi$.
 (3) It introduces the idea of stationary states.
 (4) It explains the line spectrum of hydrogen.

25. Which of the following gave the idea of nucleus of the atom?

- (1) Oil drop experiment
 (2) Davisson and Germer's experiment
 (3) α -ray scattering experiment
 (4) Austen's mass spectrogram experiment

26. A cricket ball of 0.5 kg is moving with a velocity of 100 m s^{-1} . The wavelength associated with its motion is

- (1) $1/100 \text{ cm}$ (2) $66 \times 10^{-34} \text{ m}$
 (3) $1.32 \times 10^{-35} \text{ m}$ (4) $6.6 \times 10^{-28} \text{ m}$

27. In hydrogen spectrum, the series of lines appearing in ultra violet region of electromagnetic spectrum are called

- (1) Balmer lines (2) Lyman lines
 (3) Pfund lines (4) Brackett lines

28. The transition in He^+ ion that would have the same wavelength as the first Lyman line in hydrogen spectrum is

- (1) $2 \rightarrow 1$ (2) $5 \rightarrow 3$ (3) $4 \rightarrow 2$ (4) $6 \rightarrow 4$

29. The work function of a metal is 4.2 eV. If radiations of 2000 Å fall on the metal, then the kinetic energy of the fastest photoelectron is:

- (1) $1.6 \times 10^{-19} \text{ J}$ (2) $16 \times 10^{10} \text{ J}$
 (3) $3.2 \times 10^{-19} \text{ J}$ (4) $6.4 \times 10^{-10} \text{ J}$

30. A certain metal when irradiated to light ($\nu = 3.2 \times 10^{16} \text{ Hz}$) emits photoelectrons with twice kinetic energy as did photoelectrons when the same metal is irradiated by light ($\nu = 2.0 \times 10^{16} \text{ Hz}$). The ν_0 (threshold frequency) of metal is

- (1) $1.2 \times 10^{14} \text{ Hz}$ (2) $8 \times 10^{15} \text{ Hz}$
 (3) $1.2 \times 10^{16} \text{ Hz}$ (4) $4 \times 10^{12} \text{ Hz}$

31. The number of spherical nodes in 4s orbital is

- (1) 4 (2) ∞ (3) 2 (4) 3

32. Which of the following orbitals does not have the angular node?

- (1) p_x -orbital (2) d_{z^2} -orbital
 (3) p_y -orbital (4) 1s-orbital

33. The ratio of the radii of the three Bohr orbits is

- (1) 1:1/2:1/3 (2) 1:2:3
 (3) 1:4:9 (4) 1:8:27

34. How many electrons in an atom with atomic number 105 can have $(n+l) = 8$?

- (1) 30 (2) 17
 (3) 15 (4) Unpredictable

35. If the threshold wavelength (λ_0) for ejection of electron from metal is 330 nm, then work function for the photoelectric emission is

- (1) $1.2 \times 10^{-18} \text{ J}$ (2) $1.2 \times 10^{-20} \text{ J}$
 (3) $6 \times 10^{-19} \text{ J}$ (4) $6 \times 10^{-12} \text{ J}$

36. The heaviest subatomic particle is

- (1) Neutron (2) Positron
 (3) Electron (4) Proton

37. The line spectrum of two elements is not identical because

- (1) They do not have same number of neutrons
 (2) They have dissimilar mass number
 (3) They have different energy level schemes
 (4) They have different number of valence electrons

38. Bohr's atomic model can explain the spectrum of

- (1) Hydrogen atoms only
 (2) Atoms or ions which are unielectron
 (3) Atoms or ions which have only two electrons
 (4) Hydrogen molecule

39. The electronic configuration of a diapositive ion M^{2+} is 2, 8, 14 and its mass number is 56. The number of neutrons present is

- (1) 32 (2) 42 (3) 30 (4) 34

40. The kinetic energy of the photoelectrons does not depend upon
 (1) Intensity of incident radiation
 (2) Frequency of incident radiation
 (3) Wavelength of incident radiation
 (4) Wave number of incident radiation.
41. The experimental evidence for dual nature of matter comes from
 (1) Planck's experiment
 (2) de Broglie's experiment
 (3) Davison and Germer's experiment
 (4) Rutherford's experiment
42. In excited H atom, when electron drops from $n = 4, 5, 6$ to $n = 1$, there is emission of
 (1) UV light (2) Visible light
 (3) IR light (4) Radio waves
43. When two electrons are placed in two degenerate orbitals of the atom, the energy is lower if their spin is parallel. The statement is based upon
 (1) Pauli's exclusion (2) Bohr's rule
 (3) Hund's rules (4) Aufbau principle
44. The wave mechanical model of an atom is based upon which of the following equations?
 (1) Schrödinger's equation
 (2) de Broglie's equation
 (3) Heisenberg's uncertainty principle
 (4) All the above
45. An orbital with $l = 0$ is
 (1) Symmetrical about X-axis only
 (2) Symmetrical about Y-axis only
 (3) Spherically symmetrical
 (4) Unsymmetrical
46. For a given principal level $n = 4$, the energy of its subshells is of the order
 (1) $s < d < f < p$ (2) $s < p < d < f$
 (3) $d < f < p < s$ (4) $s < p < f < d$
47. Sodium chloride imparts a yellow colour to the Bunsen flame. This can be interpreted due to the
 (1) Low ionisation energy of sodium.
 (2) Sublimation of metallic sodium to give yellow vapour.
 (3) Emission of excess energy absorbed as a radiation in the visible region
 (4) Photosensitivity of sodium
48. How many unpaired electrons are there in Ni^{2+} ?
 (1) 0 (2) 2 (3) 4 (4) 8
49. The exact path of electron $2p$ orbital cannot be determined. the above statement is based upon
 (1) Hund's rule
 (2) Bohr's rule
 (3) Uncertainty principle
 (4) Aufbau principle
50. For the energy levels in an atom, which one of the following statement is correct?
 (1) There are seven principal electron energy levels.
 (2) The second principal energy level has four sub-energy levels and contain a maximum of eight electrons.
 (3) The principal energy level N can have a maximum of 32 electrons.
 (4) The $4s$ sub-energy level has high energy than $3d$ subenergy level.
51. Any p orbital can accommodate up to
 (1) Four electrons
 (2) Two electrons with parallel spin
 (3) Six electrons
 (4) Two electrons with opposite spin
52. The magnetic quantum number of an atom is related to the
 (1) Size of the orbital
 (2) Spin angular momentum
 (3) Orbital angular momentum
 (4) Orientation of the orbital in space
53. Rutherford's scattering experiment is related to the size of the
 (1) Nucleus (2) Atom (3) Electron (4) Neutron
54. The number of spherical nodes in $3p$ orbital are:
 (1) One (2) Three (3) None (4) Two
55. The ratio of energy of photon of $\lambda = 2000 \text{ \AA}$ to that of $\lambda = 4000 \text{ \AA}$ is
 (1) 2 (2) $1/4$ (3) 4 (4) $1/2$
56. If r is radius of first orbit, the radius of n th orbit of the H atom will be
 (1) rn^2 (2) rn (3) r/n (4) r^2n^3
57. The energy of hydrogen atom in its ground state is -13.6 eV . The energy of the level corresponding to the quantum number $n = 5$ is
 (1) -0.54 eV (2) -5.40 eV (3) -0.85 eV (4) -2.72 eV
58. At 200°C , hydrogen molecules have velocity $2.4 \times 10^3 \text{ m s}^{-1}$. The de Broglie wavelength in this case is approximately
 (1) 1 \AA (2) 1000 \AA (3) 100 \AA (4) 10 \AA
59. Which combinations of quantum number n, l, m, s , for the electron in an atom does not provide a permissible solution of the wave equation?
 (1) 3, 2, $-2, 1/2$ (2) 3, 3, $1, -1/2$
 (3) 3, 2, $1, 1/2$ (4) 3, 1, $1, -1/2$
60. The wave number of the first line of Balmer series of hydrogen is 15200 cm^{-1} . The wave number of the first Balmer line of Li^{2+} ion is
 (1) 15200 cm^{-1} (2) 60800 cm^{-1}
 (3) 76000 cm^{-1} (4) 136800 cm^{-1}
61. The radius of second Bohr's orbit is
 (1) 0.053 nm (2) $\frac{0.053}{4} \text{ nm}$
 (3) $0.053 \times 4 \text{ nm}$ (4) $0.053 \times 20 \text{ nm}$

62. The set of quantum numbers not applicable to an electron
 (1) 1, 1, 1, +1/2 (2) 1, 0, 0, +1/2
 (3) 1, 0, 0, -1/2 (4) 2, 0, 0, +1/2
63. The number of spectral lines obtained in Bohr spectrum of hydrogen atom when an electron is excited from ground level to 5th orbit is
 (1) 10 (2) 5 (3) 8 (4) 15
64. In the above question (Q. 63), the number of spectral lines obtained in Bohr spectrum of hydrogen atom when an electron is excited from 2nd orbit to 5th orbit, is
 (1) 3 (2) 6 (3) 10 (4) 5
65. Among the following transitions in hydrogen and hydrogen-like ion spectrum, which one emits light of longest wavelength?
 (1) $n = 2$ to $n = 1$ for H (2) $n = 4$ to $n = 3$ for Li^{2+}
 (3) $n = 4$ to $n = 3$ for He^{\oplus} (4) $n = 5$ to $n = 2$ for H
66. A photon of frequency ν causes photoelectric emission from a surface with threshold frequency ν_0 . The de Broglie wavelength λ of the photoelectron emitted is given as
 (1) $\Delta n = \frac{h}{2m\lambda}$ (2) $\Delta n = \frac{h}{\lambda}$
 (3) $\left[\frac{1}{\nu_0} - \frac{1}{\nu} \right] = \frac{mc^2}{h}$ (4) $\lambda = \sqrt{\frac{h}{2m\Delta n}}$
67. The important principles that do not help in assigning electronic configuration to atoms are
 (1) Aufbau rule
 (2) Hund's rule
 (3) Heisenberg uncertainty principle
 (4) Pauli's exclusion principle
68. The total spin and magnetic moment for the atom with atomic number 7 are:
 (1) $\pm 3, \sqrt{3}$ BM (2) $\pm 1, \sqrt{8}$ BM
 (3) $\pm \frac{3}{2}, \sqrt{15}$ BM (4) $0, \sqrt{8}$ BM
69. The total spin and magnetic moment for the atom with atomic number 24 are:
 (1) $\pm 3, \sqrt{48}$ BM (2) $\pm 3, \sqrt{35}$ BM
 (3) $\pm \frac{3}{2}, \sqrt{48}$ BM (4) $\pm \frac{3}{2}, \sqrt{35}$ BM
70. A neutral atom of an element has 2K, 8L, 9M, and 2N electrons. The atomic number of element is:
 (1) 20 (2) 21 (3) 22 (4) 23
- For Problems 71–75, follow Q. 70**
71. The total number of s electrons are
 (1) 8 (2) 6 (3) 4 (4) 10
72. The total number of p-electrons are
 (1) 6 (2) 12 (3) 18 (4) 24
73. The total number of d-electrons are
 (1) 1 (2) 2 (3) 3 (4) 4
74. The total number of unpaired electrons are
 (1) 1 (2) 2 (3) 3 (4) 4
75. The valency of element is
 (1) +2 (2) +3
 (3) Both +2 and +3 (4) +1
76. An oxide of N has vapour density 46. Find the total number of electrons in its 92 g. (N_A = Avogadro's number)
 (1) $46N_A$ (2) $38N_A$ (3) $54N_A$ (4) $30N_A$
77. The angular momentum of an electron in 4s orbital, 3p orbital, and 4th orbit are
 (1) $0, \frac{1}{\sqrt{2}} \frac{h}{\pi}, \frac{2h}{\pi}$ (2) $\frac{1}{\sqrt{2}} \frac{h}{\pi}, \frac{2h}{\pi}, 0$
 (3) $0, \frac{\sqrt{2}h}{\pi}, \frac{4h}{\pi}$ (4) $\frac{\sqrt{2}h}{\pi}, \frac{4h}{\pi}, 0$
78. The decreasing order of energy for the electrons represented by the following sets of quantum numbers is
 1. $n = 4, l = 0, m = 0, s = \pm 1/2$
 2. $n = 3, l = 1, m = 1, s = -1/2$
 3. $n = 3, l = 2, m = 0, s = +1/2$
 4. $n = 3, l = 0, m = 0, s = -1/2$
 (1) $1 > 2 > 3 > 4$ (2) $2 > 1 > 3 > 4$
 (3) $3 > 1 > 2 > 4$ (4) $4 > 3 > 2 > 1$
79. ${}^7_4\text{Be}$ captures a K electron into its nucleus. What is the mass number and atomic number of the nuclide formed?
 (1) 3, 7 (2) 4, 8 (3) 3, 8 (4) 4, 7
80. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^{\oplus} spectrum?
 (1) $n_1 = 1$ to $n_2 = 2$ (2) $n_1 = 2$ to $n_2 = 4$
 (3) $n_1 = 1$ to $n_2 = 3$ (4) $n_1 = 2$ to $n_2 = 3$
81. The wavelength of H_{α} line of Balmer series is $X \text{ \AA}$. What is the X of H_{β} line of Balmer series.
 (1) $X \frac{108}{80} \text{ \AA}$ (2) $X \frac{80}{108} \text{ \AA}$
 (3) $\frac{1}{X} \frac{80}{108} \text{ \AA}$ (4) $\frac{1}{X} \frac{108}{80} \text{ \AA}$
82. The shortest and longest wave number in H_{γ} spectrum of Lyman series is (R = Rydberg constant)
 (1) $\frac{3}{4} R, R$ (2) $\frac{1}{R}, \frac{4}{3} R$
 (3) $R, \frac{4}{3} R$ (4) $R, \frac{3}{4} R$
83. The radius of the second Bohr orbit for Li^{2+} is
 (1) $0.529 \times \frac{4}{3} \text{ \AA}$ (2) $0.529 \times \frac{2}{3} \text{ \AA}$
 (3) $0.529 \times \frac{4}{9} \text{ \AA}$ (4) $0.529 \times \frac{2}{9} \text{ \AA}$
84. The radius of the first Bohr orbit for He^{\oplus} is
 (1) 0.529 \AA (2) 0.264 \AA (3) 0.132 \AA (4) 0.176 \AA
85. In an oil drop experiment, the following charges (in arbitrary units) were found on a series of oil droplets

$$2.30 \times 10^{-15}, 6.90 \times 10^{-15}, 1.38 \times 10^{-14}$$

$$5.75 \times 10^{-15}, 3.45 \times 10^{-15}, 1.96 \times 10^{-14}$$

The magnitude of charge on the electron (in the same unit) is

$$(1) 1.15 \times 10^{-15} \quad (2) 2.30 \times 10^{-15}$$

$$(3) 0.575 \times 10^{-15} \quad (4) 1.96 \times 10^{-14}$$

86. In what ratio should ${}_{17}\text{Cl}^{37}$ and ${}_{17}\text{Cl}^{35}$ be present so as to obtain ${}_{17}\text{Cl}^{35.5}$?

$$(1) 1:2 \quad (2) 1:1 \quad (3) 1:3 \quad (4) 3:1$$

87. Which of the following relates to photon both as wave motion and as a stream of particles?

$$(1) \text{Interference} \quad (2) E = mc^2$$

$$(3) \text{Diffraction} \quad (4) E = h\nu$$

88. Which of the following sets of quantum numbers is not correctly represented in case of the indicated spectral series of hydrogen atom?

$$(1) \text{Lyman series } n_1 = 1; \quad n_2 = 2, 3, 4, \dots$$

$$(2) \text{Balmer series } n_1 = 2; \quad n_2 = 3, 4, 5, \dots$$

$$(3) \text{Paschen series } n_1 = 3; \quad n_2 = 4, 5, 6, \dots$$

$$(4) \text{Brackett series } n_1 = 4; \quad n_2 = 5, 6, 7, \dots$$

89. If Aufbau rule is not followed in filling of suborbitals, then block of the element will change in

$$(1) \text{K (19)} \quad (2) \text{Sc (21)} \quad (3) \text{V (23)} \quad (4) \text{Ni (28)}$$

90. If Hund's rule is not followed, magnetic moment of Fe^{2+} , Mn^{2+} , and Cr^{3+} all having 24 electrons will be in order

$$(1) \text{Fe}^{2+} < \text{Mn}^{2+} < \text{Cr}^{3+} \quad (2) \text{Fe}^{2+} = \text{Cr}^{3+} < \text{Mn}^{2+}$$

$$(3) \text{Fe}^{2+} = \text{Mn}^{2+} < \text{Cr}^{3+} \quad (4) \text{Mn}^{2+} = \text{Cr}^{3+} < \text{Fe}^{2+}$$

91. If wavelength is equal to the distance travelled by the electron in one second, then

$$(1) \lambda = h/p \quad (2) \lambda = h/m \quad (3) \lambda = \sqrt{h/p} \quad (4) \lambda = \sqrt{h/m}$$

92. The ratio of kinetic energy and potential energy of an electron in a Bohr orbit of a hydrogen-like species is

$$(1) 1/2 \quad (2) -1/2 \quad (3) 1 \quad (4) -1$$

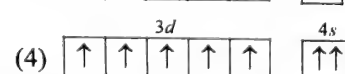
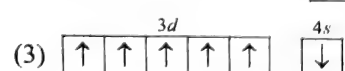
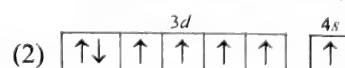
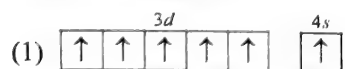
93. The ratio of kinetic energy and total energy of an electron in a Bohr orbit of a hydrogen-like species is

$$(1) 1/2 \quad (2) -1/2 \quad (3) 1 \quad (4) -1$$

94. The ratio of potential energy and total energy of an electron in a Bohr orbit of a hydrogen-like species is

$$(1) 2 \quad (2) -2 \quad (3) 1 \quad (4) -1$$

95. Which of the following arrangements of electrons is mostly likely to be stable?



96. If velocity of an electron in 1st orbit of H atom is V , what will be the velocity in 3rd orbit of Li^{2+} ?

$$(1) V \quad (2) \frac{V}{3} \quad (3) 3V \quad (4) 9V$$

97. The energy of an electron in the first Bohr orbit for hydrogen is -13.6 eV . Which one of the following is a possible excited state for electron in Bohr orbit of hydrogen atom?

$$(1) -3.4 \text{ eV} \quad (2) -6.8 \text{ eV} \quad (3) -1.7 \text{ eV} \quad (4) 13.6 \text{ eV}$$

98. The spectral line obtained when an electron jumps from $n = 6$ to $n = 2$ level in hydrogen atom belongs to the

$$(1) \text{Balmer series} \quad (2) \text{Lyman series}$$

$$(3) \text{Paschen series} \quad (4) \text{Pfund series}$$

99. Which of the following species will produce the shortest wavelength for the transition $n = 2$ to $n = 1$?

$$(1) \text{Hydrogen atom}$$

$$(2) \text{Singly ionised helium}$$

$$(3) \text{Deuterium atom}$$

$$(4) \text{Doubly ionised lithium}$$

100. The ionisation potential of hydrogen atom is 13.6 eV . The energy required to remove an electron in the $n = 2$ state of the hydrogen atom is

$$(1) 3.4 \text{ eV} \quad (2) 6.8 \text{ eV}$$

$$(3) 13.6 \text{ eV} \quad (4) 27.2 \text{ eV}$$

101. If the wavelength of the first line of the Balmer series of hydrogen atom is 656.1 nm , the wavelength of the second line of this series would be

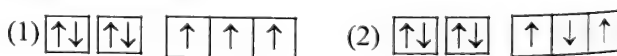
$$(1) 218.7 \text{ nm} \quad (2) 328.0 \text{ nm}$$

$$(3) 486.0 \text{ nm} \quad (4) 640.0 \text{ nm}$$

102. The energy of an electron in the first Bohr orbit of H atom is -13.6 eV . The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are)

$$(1) -3.4 \text{ eV} \quad (2) -4.2 \text{ eV} \quad (3) -6.8 \text{ eV} \quad (4) +6.8 \text{ eV}$$

103. Ground state electronic configuration of nitrogen atom can be represented by



104. The electronic configuration of an element is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This represents its

$$(1) \text{Excited state} \quad (2) \text{Ground state}$$

$$(3) \text{Cationic form} \quad (4) \text{Anionic form}$$

105. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m h^{-1} is of the order

$$(1) 10^{-10} \text{ m} \quad (2) 10^{-20} \text{ m} \quad (3) 10^{-30} \text{ m} \quad (4) 10^{-40} \text{ m}$$

106. Rutherford's experiment, which established the nuclear model of the atom, used a beam of

$$(1) \beta\text{-particles, which impinged on a metal foil and got absorbed.}$$

$$(2) \gamma\text{-rays, which impinged on a metal foil and ejected electrons.}$$

$$(3) \text{Helium atom, which impinged on a metal foil and got scattered.}$$

$$(4) \text{Helium nuclei, which impinged on a metal foil and got scattered.}$$

107. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is

- (1) $[\text{Ne}]3s^2 3p^1$ (2) $[\text{Ne}]3s^2 3p^3$
 (3) $[\text{Ne}]3s^2 3p^2$ (4) $[\text{Ar}]3d^{10} 4s^2 4p^3$

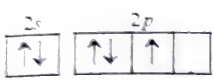

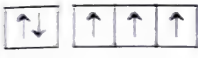

108. The correct ground state electronic configuration of chromium atom is

- (1) $[\text{Ar}]3d^5 4s^1$ (2) $[\text{Ar}]3d^4 4s^2$
 (3) $[\text{Ar}]3d^6 4s^0$ (4) $[\text{Ar}]4d^5 4s^1$

109. The correct set of quantum numbers for the unpaired electron of chlorine atom is

- | | n | l | m_l | | n | l | m_l |
|-----|-----|-----|-------|-----|-----|-----|-------|
| (1) | 2 | 1 | 0 | (2) | 2 | 1 | 1 |
| (3) | 3 | 1 | 1 | (4) | 3 | 0 | 0 |

110. The orbital diagram in which the Aufbau principle is violated is

- (1) 
- (2) 
- (3) 
- (4) 

111. The first ionisation potential in electron volts of nitrogen and oxygen atoms are, respectively, given by

- (1) 14.6, 13.6 (2) 13.6, 14.6
 (3) 13.6, 13.6 (4) 14.6, 14.6

112. Atomic radii of fluorine and neon in Angstrom units are respectively given by

- (1) 0.72, 1.60 (2) 1.60, 1.60
 (3) 0.72, 0.72 (4) None of these

113. The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000 Å radiation is

- (1) 1/4 (2) 4 (3) 1/2 (4) 2

114. The sum of the number of neutrons and proton in the isotope of hydrogen is

- (1) 6 (2) 5 (3) 4 (4) 3

115. The radius of an atomic nucleus is of the order of

- (1) 10^{-16} cm (2) 10^{-13} cm
 (3) 10^{-15} cm (4) 10^{-8} cm

116. Which of the following is true?

- (1) The outer electronic configuration of the ground state chromium atom is $3d^4 4s^2$.
 (2) Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} cm to 10^{-5} cm.
 (3) The energy of the electron in the 3d orbital is less than that in the 4s orbital of a hydrogen atom.
 (4) The electron density in the xy-plane in $3d_{x^2-y^2}$ orbital is zero.

117. Which of the following is true?

- (1) Diapositive zinc exhibits paramagnetism due to loss of two electrons from a 3d orbital of neutral atom.

(2) In β -emission from a nucleus, the atomic number of the daughter element decreases by 1.

(3) The emission of one α -particle from a radioactive atom results in the decrease of atomic number by 2 and mass number by 4.

(4) The successive emission of two β -particles from a radioactive atom results in the decrease of atomic number by 1.

118. Which of the following is true?

(1) Neutrino is a positively charged electron.

(2) The magnetic moment of an atom is related to the number of unpaired electrons in its electronic configuration.

(3) Bohr theory can be successfully modified to explain the electronic spectrum of multielectron atom.

(4) The angular momentum of an electron in an atom is given as $n\left(\frac{h}{2\pi}\right)$.

119. Which of the following is false?

(1) The angular momentum of an electron due to its spinning is given as $\sqrt{s(s+1)}\left(\frac{h}{2\pi}\right)$, where s can take a value of 1/2.

(2) The angular momentum of an electron due to its spinning is given as $m_s\left(\frac{h}{2\pi}\right)$, where m_s can take the value of +1/2.

(3) The azimuthal quantum number cannot have negative values.

(4) The potential energy of an electron in an orbit is twice in magnitude as compared to its kinetic energy.

120. Which of the following is true?

(1) According to Pauli's exclusion principle, no two electrons in an atom can have the same values of quantum numbers n , l , and m .

(2) The total energy of an electron in an orbit is half of its potential energy.

(3) The speed of an electron in a orbit increases with increase of its quantum number n .

(4) The energy of an electron in a orbit decreases with increase of its quantum number n .

121. Which of the following is true?

(1) The ionisation energy of a hydrogen-like species in its ground state is equal to the magnitude of energy of the orbit having $n = 1$.

(2) The ionisation energy of a hydrogen-like species in its ground state increases in proportion to the positive charge in its nucleus.

(3) According to the uncertainty principle, $\Delta p \Delta x \leq \frac{h}{4\pi}$.

(4) The energy of an electron in an orbital of a multielectron atom depends only on the principal quantum number n .

122. Which of the following is false?

- (1) The energy of an electron in an orbital of a hydrogen-like species depends only on the principal quantum number n .
- (2) The angular momentum of an electron in an orbital of a multielectron atom depends on the quantum numbers l and m .
- (3) The expression of angular momentum of an electron in an orbital is given as $\sqrt{l(l+1)} \left(\frac{h}{2\pi} \right)$.
- (4) The z -component of angular momentum of an electron in an orbital is given as $m \left(\frac{h}{2\pi} \right)$.

123. Which of the following is false?

- (1) The number of orbitals for a given value of l is equal to $2l + 1$.
- (2) The number of orbitals for a given value of n is equal to n^2 .
- (3) An atom having unpaired electrons is diamagnetic in nature.
- (4) All s orbitals are spherical symmetrical in shape.

124. Which of the following is true?

- (1) The half-filled and fully-filled electronic configurations are less stable than the other configurations having the same number of electrons.
- (2) The symbol s for the orbitals having $l = 0$ has its origin from the term spherical symmetrical.
- (3) The increasing order for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n), and alpha particle (α) is $n < \alpha < p < e$.
- (4) The energy of photon having wavelength 800 nm is larger than that having 400 nm.

125. Which of the following is false?

- (1) Pfund spectral series for which $n_1 = 5$ and $n_2 = 6, 7, \dots$ lies in the far infrared region of the electromagnetic radiation.
- (2) Visible region of electromagnetic radiations has wavelength from 400 nm to 800 nm.
- (3) Balmer spectral series lies in the visible portion of the electromagnetic radiation.
- (4) Lyman spectral series lies in the visible portion of the electromagnetic radiation.

126. Which of the following is false?

- (1) Brackett spectral series for which $n_1 = 4$ and $n_2 = 5, 6, 7, \dots$ lies in the infrared region of the electromagnetic radiation.
- (2) The orbital $3d_{z^2}$ is symmetrical about z -axis.
- (3) The orbital $3d_{xy}$ has no probability of finding electron along x - and y -axis.
- (4) The orbital $3d_{x^2-y^2}$ has no probability of finding electron along x - and y -axis.

127. Which of the following is true?

- (1) The electron density in the xy -plane in $3d_{xy}$ orbital is zero.
- (2) The electron densities in the xy - and xz -plane in $3d$ orbital are zero.
- (3) The electron density in the xy -plane in $3d_{z^2}$ orbital is zero.
- (4) Pauli exclusion principle is followed by bosons which have integral spin.

128. Which of the following is false?

- (1) The d orbitals are no more degenerate in the presence of a magnetic field.
- (2) The spin quantum number was introduced to explain the splitting of spectral lines of hydrogen atom in the presence of a magnetic field.
- (3) Pauli exclusion principle is followed by fermions which have half integral spins.
- (4) The energy of an orbital in an atom remains the same with increase in the positive charge in its nucleus.

Multiple Correct Answers Type

1. Which of the following statements are correct?

- (1) The electronic configuration of Cr is $[\text{Ar}]3d^5, 4s^1$ (atomic number of Cs = 24).
- (2) The magnetic quantum number may have a negative value.
- (3) In Silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47)
- (4) The oxidation state of nitrogen in NH_3 is -3 .

2. Ground state electronic configuration of nitrogen atom can be represented as

- (1) $\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\uparrow\uparrow$
- (2) $\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow\uparrow$
- (3) $\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow\downarrow$
- (4) $\uparrow\downarrow \quad \uparrow\downarrow \quad \downarrow\downarrow\downarrow$

3. Which of the following orbitals has(have) one spherical node?

- (1) $1s$ (2) $2s$ (3) $2p$ (4) $3p$

4. The energy of an electron in the first energy level of H atom is -13.6 eV. The possible energy value(s) of the excited state(s) for the electron in He^+ is (are).

- (1) -54.4 eV (2) -13.6 eV (3) -3.4 eV (4) -6.4 eV

5. Which of the following species has (have) five unpaired electrons?

- (1) Cs (2) Mn (3) Mn^{2+} (4) Fe^{2+}

6. Which of the following series in H-spectra occurs in IR region.

- (1) Lyman (2) Paschen (3) Brackett (4) Balmer

7. Which of the following elements are isotopes.
 (1) C^{12} (2) C^{13} (3) C^{14} (4) N^{14}
8. Which of the following properties are possessed by cathode ray?
 (1) Dual nature (2) Travel with speed of light
 (3) Have negative charge (4) Possess magnetic effect
9. Which of the following are isotones?
 (1) $^{40}_{18}\text{Ar}$ (2) $^{42}_{20}\text{Ca}$ (3) $^{43}_{21}\text{Sc}$ (4) $^{41}_{21}\text{Sc}$
10. The energy of an electron in the first Bohr orbit of H atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electron in Bohr orbits of hydrogen is(are).
 (1) -3.4 eV (2) 4.2 eV (3) -6.8 eV (4) $+6.8$ eV
11. When α -particles are sent through a thin metal foil, most of them go straight through the foil because,
 (1) α -particles are much heavier than electrons
 (2) α -particles are positively charged
 (3) Most part of the atom is empty space
 (4) α -particles move with high speed
12. Which of the following sets of quantum number is/are not permitted?
 (1) $n = 3, l = 3, m = +1, s = +\frac{1}{2}$
 (2) $n = 3, l = 2, m = +2, s = -\frac{1}{2}$
 (3) $n = 3, l = 1, m = +2, s = -\frac{1}{2}$
 (4) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$
13. The lightest particle is/are
 (1) Electron (2) Proton (3) Neutron (4) β -particle
14. Which orbital of the following is lower in energy in a many electron atom?
 (1) $2p$ (2) $3d$ (3) $4s$ (4) $5f$
15. Which of the following statement(s) is/are correct?
 (1) Electrons behaves as a wave.
 (2) s -orbital is non-directional.
 (3) An orbital can accommodate a maximum of two electrons with parallel spins.
 (4) The energies of the various sub-shells in the same shell are in the order $s > p > d > f$.
16. The angular momentum of p electron is
 (1) $\frac{h}{2\pi}\sqrt{6}$ (2) $\hbar\sqrt{6}$ (3) $\hbar\sqrt{2}$ (4) $\frac{h}{2\pi}\sqrt{2}$
17. The angular momentum of P electron is
 (1) $\frac{h}{2\pi}\sqrt{6}$ (2) $\hbar\sqrt{2}$ (3) $\frac{h}{2\pi}\sqrt{2}$ (4) $\hbar\sqrt{6}$
18. Which of the following is/are possible?
 (1) $3f$ (2) $4d$ (3) $2d$ (4) $3p$
19. If the value of $(n + l)$ is more than 3 and less than 6, then what will be the possible number of orbitals?
 (1) 6 (2) 9 (3) 10 (4) 13
20. Which of the following is/are not indicated by the sign of lobes in an atom?
 (1) Sign of charges
 (2) Sign of probability distribution
 (3) Sign of wave function
 (4) Presence or absence of electron
21. Which of the following does not relate to photon both as wave motion and as stream of particles?
 (1) $E = h\nu$ (2) $E = mc^2$
 (3) Interference (4) Diffraction
22. What transition in He^+ ion shall have the same wave number as the first line in Balmer series of H atom?
 (1) $7 \rightarrow 5$ (2) $6 \rightarrow 4$ (3) $5 \rightarrow 3$ (4) $4 \rightarrow 2$
23. An electron has spin quantum number (s) $+1/2$ and magnetic quantum number is -1 . It can be present in
 (1) s orbital (2) d orbital
 (3) p orbital (4) f orbital
24. The radial part of wave function depends on the quantum numbers
 (1) n (2) l (3) l, m_l (4) n only
25. How many spherical nodes are present in $4s$ orbital in a hydrogen atom?
 (1) 0 (2) 2 (3) 3 (4) 4
26. Which of the following statement about quantum number is correct?
 (1) If the value of $l = 0$, the electron distribution is spherical.
 (2) The shape of orbital is given by subsidiary quantum number.
 (3) The Zeeman's effect is explained by magnetic quantum number.
 (4) The spin quantum number gives the orientations of electron cloud.
27. A hydrogen-like atom in ground state absorbs n photons having the same energy and its emits exactly n photons when electrons transition takes place. Then, the energy of the absorbed photon may be
 (1) 91.8 eV (2) 40.8 eV (3) 48.4 eV (4) 54.4 eV
28. Magnetic moment of $\text{V}(Z = 23)$, $\text{Cr}(Z = 24)$, and $\text{Mn}(Z = 25)$ are x, y, z , respectively, hence
 (1) $x = y = z$ (2) $x < y < z$ (3) $x < z < y$ (4) $z < y < x$
29. Consider the ground state of Cr atom ($Z = 24$). The number of electrons with the azimuthal quantum number, $l = 1$ and 2 , respectively, are
 (1) 16 and 5 (2) 12 and 5 (3) 16 and 5 (4) 12 and 4
30. When an electron makes a transition from $(n + 1)$ state to n state, the frequency of emitted radiations is related to n according to $(n \gg 1)$.
 (1) $\nu \propto n^{-3}$ (2) $\nu \propto n^2$ (3) $\nu \propto n^3$ (4) $\nu \propto n^{\frac{3}{2}}$
31. In a sample of H-atoms, electrons make transitions from $n = 5$ to $n = 1$. If all the spectral lines are observed, then the line having the third highest energy will correspond to
 (1) $5 \rightarrow 3$ (2) $4 \rightarrow 1$ (3) $3 \rightarrow 1$ (4) $5 \rightarrow 4$

32. Rutherford's α -scattering experiment led to the following conclusions:
- (1) Atom has largely empty space.
 - (2) The centre of the atom has positively charged nucleus.
 - (3) The size of the nucleus is very small as compared to the size of the atom.
 - (4) Electrons revolve around the nucleus.
33. The probability of finding the electron in p_x orbital is
- (1) Maximum on two opposite sides of the nucleus along X-axis.
 - (2) Zero at the nucleus
 - (3) They produce heating effect
 - (4) They can affect photographic plate
34. Which of the following statements concerning Bohr's model is are true?
- (1) It predicts that probability of electron near nucleus is more
 - (2) Angular momentum of electron in H atom = $nh/2\pi$.
 - (3) It introduces the idea of stationary states.
 - (4) It explains line spectrum of hydrogen.
35. Which sets of quantum number are consistent with the theory?
- (1) $n = 2, l = 1, m = 0, s = -1/2$
 - (2) $n = 4, l = 3, m = -2, s = -1/2$
 - (3) $n = 3, l = 2, m = -3, s = +1/2$
 - (4) $n = 4, l = 3, m = -3, s = +1/2$
36. An electron is not deflected on passing through a certain region because
- (1) There is no magnetic field in that region
 - (2) There is a magnetic field but velocity of the electron is parallel to the direction of magnetic field
 - (3) The electron is a chargeless particle
 - (4) None of the above
37. Heisenberg uncertainty principle is not valid for
- (1) Moving electrons
 - (2) Motor car
 - (3) Stationary particles
 - (4) All of the above
38. Which of the following statements are correct for an electron that has $n = 4$ and $m = -2$?
- (1) The electron may be in a d -orbital.
 - (2) The electron is in the fourth principal electronic shell
 - (3) The electron may be in a p -orbital.
 - (4) The electron must have the spin quantum number = $+1/2$.
39. The wave nature of electron was verified by
- (1) de Broglie
 - (2) Davisson and Germer
 - (3) G.P. Thomson
 - (4) Rutherford
40. Which of the following statements is/are correct?
- (1) There is no probability of finding a p -electron right at the nucleus.
 - (2) The orbital d_{z^2} has two lobes of electron density directed along the z -axis and a ring of electron density (called dough nut) centred in the xy -plane.
 - (3) The orientation of p and d orbitals minimises electron-electron repulsion in many electron atoms.
 - (4) None is correct.
41. Which of the following statements is/are correct?
- (1) For all values of n , the p orbitals have the same shape, but the overall size increases as n increase, for a given atom.
 - (2) The fact that there is a particular direction along which each p orbital has maximum electron density, plays an important role in determining molecular geometries.
 - (3) The charge cloud of a single electron in $2p_x$ atomic orbital consists of two lobes of electron density.
 - (4) None is correct.
42. The charged cloud of a single electron in a $2p_x$ atomic orbital has two lobes of electron density. This means
- (1) There is a high probability of locating the electron in the $2p_x$ atomic orbital at values of $x > 0$.
 - (2) There is a high probability of locating it at values of $x > 0$ but no probability at all of locating it anywhere in the yz -plane along which $x = 0$.
 - (3) There is a great probability of finding a p electron right at the nucleus.
 - (4) All are correct.
43. Which of the following statements is/are correct?
- (1) The energy of an electron in a many electron atom generally increases with an increase in value of n , but for a given, the lower the value of l the lower the energy
 - (2) An electron close to the nucleus experiences a large electrostatic attraction
 - (3) For a given value of n , an s -electron penetrates of the nucleus more than a p -electron, which penetrates more than a d -electron, and so on.
 - (4) None is correct
44. Which is correct statement in case of Hund's rule?
- (1) It states that if more than one atomic orbital of the same energy is available, electrons will occupy different atomic orbitals with parallel spins, as far as possible, in the configuration of lowest energy
 - (2) Total energy of many electron atom with more than one electron occupying a set of degenerate orbitals is lowest, if as far as possible, electrons occupy different atomic orbitals and have parallel spins
 - (3) Hund's rule forbid any configuration that does not violate the Pauli's exclusion principle
 - (4) Hund's rule simply tells us which of the possible configurations is lowest in energy and other configurations are those of excited states, higher in energy than the ground state
45. Which of the following is true?
- (1) A configuration with the maximum spin multiplicity has the minimum energy and thus is most stable.

- (2) The energy of $3d$ orbital may be greater than or lesser than, or equal to that of $4s$ orbital depending upon the atomic number of the atom.
- (3) All p orbitals have the same type of angular dependence irrespective of the value of principal quantum number n .
- (4) In a given electrical field, β -particles are deflected more than α -particles in spite of α -particles having larger charge.

Linked Comprehension Type

Paragraph 1

The atomic number of chromium is 24. Its electronic configuration in ground state is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$. Chromium atom by losing 3 electrons form Cr^{3+} ions. A chromium atom contains 17% more neutron than the protons. Now answer the following questions:

- The number of unpaired electrons in Cr^{3+} ion is
(1) 3 (2) 6 (3) 5 (4) 1
- The numbers of electrons having $n = 3$ and $m_l = 0$ in chromium atom is
(1) 2 (2) 5 (3) 4 (4) 1
- The group number and period of the chromium in the periodic table are, respectively,
(1) 6 and 3 (2) 5 and 3 (3) 6 and 4 (4) 5 and 4
- The chromium atom can be represented by the symbol
(1) ${}_{24}Cr^{50}$ (2) ${}_{24}Cr^{52}$ (3) ${}_{52}Cr^{24}$ (4) ${}_{50}Cr^{24}$
- The number of occupied sub-shell in Cr^{3+} ion is
(1) 3 (2) 4 (3) 5 (4) 6

Paragraph 2

A neutral atom of an element has 2K, 8L, and 5M electrons. Find out the following:

- Atomic number of neutral atom
(1) 20 (2) 18 (3) 15 (4) 25
- Number of electrons in valence shell
(1) 5 (2) 6 (3) 7 (4) 4
- Number of unpaired electrons
(1) 2 (2) 3 (3) 4 (4) 5
- Number of electrons having $n + 1 = 3$
(1) 6 (2) 8 (3) 10 (4) 4
- Maximum number of electrons having same spin
(1) 5 (2) 8 (3) 9 (4) 3

Paragraph 3

In a mixture of $H-He^{\oplus}$ gas, H atom and He^{\oplus} ions are excited to their respective first excited states. Subsequently, H atom transfers its total excitation energy to He^{\oplus} ions by collision. Assuming that Bohr model of an atom is applicable, answer the following question:

- The quantum number n of the statement finally populated in He^{\oplus} ion is
(1) 1 (2) 2 (3) 4 (4) 6

- The wavelength of the light emitted in the visible region by He^{\oplus} ions after collisions with He^{\oplus} ions is
(1) 6.0×10^7 (2) 5×10^7
(3) 4.8×10^7 (4) 3×10^7

- The ratio of the potential energy of the $n = 2$ electrons for H atom to the of He^{\oplus} ion is
(1) $1/4$ (2) $1/2$
(3) 4 (4) 3

- If each hydrogen atom in the ground state of 1.0 mol of H atoms is excited by absorbing photons of energy 8.4 eV, 12.09 eV, and 15.0 eV of energy, then the number of spectral lines emitted is equal to
(1) 5 (2) 2
(3) 3 (4) 4

- When an electron of H atom jumps from a higher to lower energy state, then

- Its potential energy decreases.
- Its kinetic energy increases.
- Its angular momentum remains unchanged.
- Wavelength of de Broglie wave associated with the electron decrease.

Paragraph 4

Consider a system containing a negatively charged pion (π^- , $m_{\pi} = 273 m_e$) orbiting around a stationary nucleus of atomic number Z . The total energy (E_n) of ion is half of its potential energy (PE_n) in n th stationary state. The motion of the pion can be assumed to be in a uniform circular motion with centripetal force given by the force of attraction between the positive nucleus and the pion. Assume that pion revolves only in the stationary states defined by the quantisation of its angular momentum about the nucleus as per Bohr's model.

- The potential energy (PE_n) of ion follows:

$$(1) PE_n \propto m_{\pi} \left(\frac{n^2}{Z} \right) \quad (2) PE \propto m_{\pi} \left(\frac{Z^2}{n^2} \right)$$

$$(3) PE_n \propto \frac{1}{m_{\pi}} \left(\frac{n^2}{Z^2} \right) \quad (4) PE_n \propto \frac{1}{m_{\pi}} \left(\frac{Z^2}{n^2} \right)$$

- Number of waves made by the pion when orbiting in third excitation state are

$$(1) 3 \quad (2) 4$$

$$(3) 3Z^2 \quad (4) 4Z^2$$

- The longest wavelength radiation emitted in the emission spectrum when the pion de-excites from $n = 3$ to ground state lies in which of the following region?

$$(1) UV \quad (2) Visible$$

$$(3) Infra-Red \quad (4) Cannot be calculated$$

- The wavelength (λ_n) of the pion orbiting in n th stationary state is given by

$$(1) \lambda_{\pi} \propto \frac{n}{m_{\pi} Z} \quad (2) \lambda_{\pi} \propto \frac{m_{\pi} n}{Z}$$

$$(3) \lambda_{\pi} \propto \frac{m_{\pi} Z}{n} \quad (4) \lambda_{\pi} \propto \frac{Z}{m_{\pi} n}$$

Paragraph 5

A hydrogen like atom (atomic number Z) is in a higher excited state of quantum number n . This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV. Determine the followings:

20. The value of atomic number (Z) is
 (1) 2 (2) 4 (3) 6 (4) 3
21. The excited state (n) of the atom is
 (1) 4 (2) 6 (3) 8 (4) 3
22. The atom during transition from $n = 1$ to $n = 2$ emit radiation in the region of
 (1) Visible (2) Infra-red (3) UV (4) None
23. The hydrogen-like atom in the above question is
 (1) Li^{2+} (2) He^+ (3) H (4) None

Paragraph 6

The characteristic X-ray wavelength for the lines of K_α series in elements X and Y are 9.87 Å and 14.6 Å, respectively. If Moseley's equation, $\sqrt{\nu} = 4.9 \times 10^7 (Z - 0.75)$ is followed:

24. The atomic number of X is
 (1) 8 (2) 10 (3) 12 (4) 16
25. The atomic number of Y is
 (1) 10 (2) 6 (3) 8 (4) 12

Paragraph 7

It is impossible to determine simultaneously the position of velocity of small microscopic particle such as electron, proton, or neutron with accuracy. This is called Heisenberg's uncertainty principle. Mathematically, it is represented as $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$. Δx is uncertainty in position. Δp is uncertainty in momentum.

26. If uncertainty in the measurement of position and momentum of an electron are equal, then uncertainty in the measurement of its velocity is approximately
 (1) $8 \times 10^{12} \text{ m s}^{-1}$ (2) $6 \times 10^{12} \text{ m s}^{-1}$
 (3) $4 \times 10^{12} \text{ m s}^{-1}$ (4) $2 \times 10^{12} \text{ m s}^{-1}$
27. If a 1.00 g body is travelling along X-axis at 100 cm s^{-1} with an uncertainty in velocity as 2 cm^{-1} . The uncertainty in its position is
 (1) $5.28 \times 10^{-30} \text{ m}$ (2) $2.64 \times 10^{-30} \text{ m}$
 (3) $1.30 \times 10^{-30} \text{ m}$ (4) $0.66 \times 10^{-30} \text{ m}$

Paragraph 8

The sequence of filling electrons in sub-shells of elements with few exceptions in d -block and f -block elements is governed by Aufbau principle followed by Hund's rule and Pauli's exclusion principle.

- (1) The electron prefers to enter into sub-shells with lower $(n + l)$ value.
 The energy for any sub-shell of an element other than hydrogen is proportional to the sum of principal quantum number (n) and angular momentum quantum number

- (2) If $(n + l)$ value is same for many sub-shells, priority of electron filling is given to the sub-shell with lowest n value.
- (3) i. Fulfilled sub shell is most stable.
 ii. Half filled sub-shell is more stable less than half filled.
28. Which pair of sub-shell has same energy for above described exceptional element under rule (a)?

- (1) $1s, 2s$ (2) $2s, 2p$ (3) $3d, 4p$ (4) $5p, 4d$
29. If Hunds rule is not obeyed by some elements given below then which atom has maximum magnetic moment.
 (1) Fe (2) Cu (3) Cr (4) Mn
30. Which element with lowest atomic number follows rule (b)?
 (1) $_{19}\text{K}$ (2) $_{24}\text{Cr}$ (3) $_{11}\text{Na}$ (4) $_{29}\text{Cu}$
31. In which element rule (c) (i) is followed?
 (1) $_{29}\text{Cu}$ (2) $_{24}\text{Cr}$ (3) $_{26}\text{Fe}$ (4) $_{25}\text{Mn}$
32. Which pair of element follow rule (c) (ii)?
 (1) Cr, Mo (2) Mn, Fe (3) Cu, Ag (4) N, P

Paragraph 9

The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy orbit depending on the amount of energy absorbed. When this electron returns to any of the lower orbits, it emits energy. Lyman series is formed when the electron returns to the lowest orbit while Balmer series is formed when the electron returns to the second orbit. Similarly, Paschen, Brackett, and Pfund series are formed when electron returns to the third, fourth, and fifth orbits from higher energy orbits, respectively.

Maximum number of lines produced when an electron jumps

from n th level to ground level is equal to $\frac{n(n-1)}{2}$.

If the electron comes back from the energy level having energy E_2 to the energy level having energy E_1 , then the difference may be expressed in terms of energy of photon as

$$E_2 - E_1 = \Delta E, \quad \lambda = hc/\Delta E$$

Since h and c are constants, ΔE corresponds to definite energy; thus, each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Wave number of line is given by the formula

$$\bar{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R is a Rydberg constant.

33. If the ionisation potential for hydrogen-like atom in a sample is 122.4 V, then the series limit of the Paschen series for this atom is

- (1) R (2) $\frac{R}{3^3}$ (3) $\frac{3^2 R}{4^3}$ (4) $3^2 R$

34. In a single isolated atom, an electron makes transition from fifth excited state to second state then maximum number of different types of photons observed is

- (1) 3 (2) 4 (3) 6 (4) 15

35. The difference in the wavelength of the second line of Lyman series and last line of bracket series in a hydrogen sample is

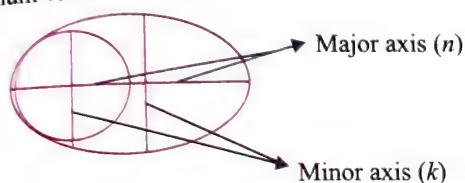
- (1) $\frac{119}{8R}$ (2) $\frac{1271}{8R}$
 (3) $\frac{219}{8R}$ (4) None of these

36. The wave number of electromagnetic radiation emitted during the transition of electron in between the two levels of Li^{2+} ion whose principal quantum numbers sum is 4 and difference is 2 is

- (1) $3.5R_H$ (2) $4R_H$ (3) $8R_H$ (4) $\frac{8}{9}R_H$

Paragraph 10

The shape of orbitals are related to the ratio of principal quantum number (n) to subsidiary quantum number (k , a modification of Bohr-Sommerfeld theory). The value of k for any shell has n value ranging between n to 1. The maximum value for k is given for s sub-shell while k becomes smaller with p, d, f, \dots respectively, upto minimum value.



If n is the major axis and k is the minor axis, then $n/k = 1$ for circular shape while $n/k > 1$ for elliptical shape.

37. Which value of n and k suggests about the shape of $3s$ orbital?

- (1) 3, 2 (2) 1, 1 (3) 3, 0 (4) 3, 3

38. The ratio of $n/k = 2$ does not related to

- (1) $2p$ (2) $4d$ (3) $6f$ (4) $2s$

39. Which shape is related to be circular having n/k value

- (1) $3/3$ (2) $4/3$ (3) $3/2$ (4) $1/2$

40. Which orbital shape has highest $n/k \gg 1$ value?

- (1) $7s$ (2) $5p$ (3) $3d$ (4) $4d$

41. Which is correct according to the increasing elliptical nature of sub-shell?

- (1) $2s < 5p < 3p < 4d$ (2) $4d < 2s < 5p < 3p$
 (3) $4d < 2s < 3p < 5p$ (4) $3p < 4d < 2s < 5p$

Paragraph 11

The emission of electrons from a metal surface when exposed to light radiation of appropriate wavelength is called photoelectric effect. The emitted electrons are called photo-electrons. Work function of threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface. According to Einstein,

$$\text{Maximum kinetic energy of ejected electron} = \text{Absorbed energy} - \text{Work function}$$

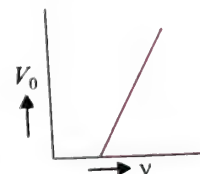
$$\frac{1}{2}mv_{\max}^2 = h(\nu) - h(\nu_0) = hc \left[\frac{1}{\lambda} - \frac{1}{\lambda_0} \right]$$

where ν_0 and λ_0 are threshold frequency and threshold wavelength, respectively.

Stopping potential: It is the minimum potential at which the photoelectric current becomes zero. If V_0 is the stopping potential $eV_0 = h(\nu - \nu_0)$.

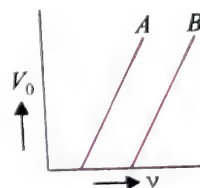
42. In the photoelectric effect, the slope of straight line graph between stopping potential (V_0) and frequency of incident light (ν) gives

- (1) charge on electron
 (2) work function of emitter
 (3) plank's constant
 (4) ratio of Planck's constant to charge on electron

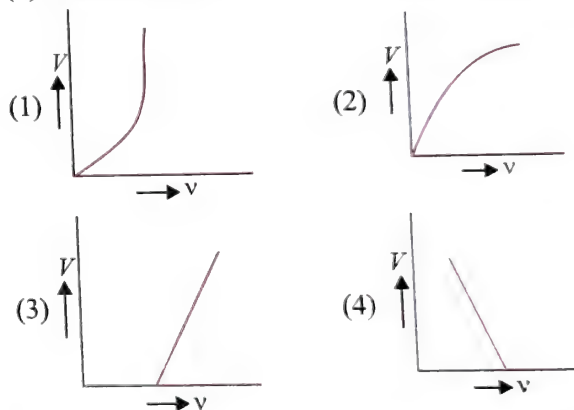


43. The stopping potential as a function of frequency is plotted for two photoelectric surfaces A and B. The graph show that the work function of A is

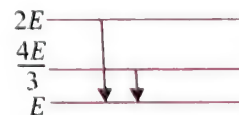
- (1) Greater than that of B
 (2) Smaller than that of B
 (3) Same as that of B
 (4) Such that no comparison can be done from given graphs



44. Which of the following is the graph between the frequency (ν) of the incident radiations and the stopping potential (V)?

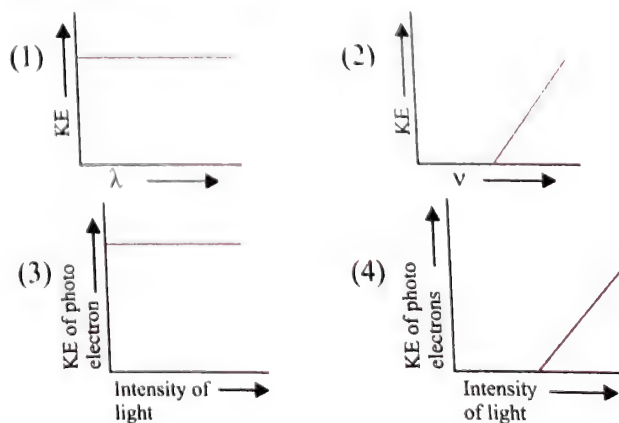


45. The following figure indicates the energy levels of a certain atom. When the system moves from $2E$ level to E level, a photon of wavelength λ is emitted. The wavelength of the photon produced during the transition from level $4E/3$ to level E is



- (1) $\frac{\lambda}{3}$ (2) $\frac{3\lambda}{4}$ (3) $\frac{4\lambda}{3}$ (4) 3λ

46. Which graph is correct?



Paragraph 12

It is tempting to think that all possible transitions are permissible and that an atomic spectrum arises from the transition of an electron from any initial orbital to any other orbital. However, this is not so, because a photon has an intrinsic spin angular momentum of $\sqrt{2} h / 2\pi$ corresponding to $S = 1$, although it has no charge and no rest mass.

On the other hand, an electron has got two types of angular momentum: orbital angular momentum,

$$L = \left[\sqrt{l(l+1)} \right] h / 2\pi, \text{ and spin angular momentum,}$$

$L_s = \sqrt{s(s+1)} h / 2\pi$ arising from orbital motion and spin motion of electron, respectively. The change in angular momentum of the electron during any electronic transition must compensate for the angular momentum carried away by the photon. To satisfy this condition the difference between the azimuthal quantum number of the orbitals within which the transition takes place must differ by 1. Thus, an electron in a d -orbital ($l = 2$) cannot make a transition into an s -orbital ($l = 0$) because the photon cannot carry away enough angular momentum.

47. Electronic transition from $4s$ to $3s$ orbital is forbidden meaning that it cannot occur, because

- (1) There will be no change in the orbital angular momentum of electron, although the emitted photon has angular momentum.
- (2) There will be change in the orbital angular momentum whereas the emitted photon has no momentum.
- (3) Δm_l values between $4s$ and $3s$ is not zero, which is an important selection rule for allowed transition
- (4) In $4s$ and $3s$ orbitals, the wavelength of the electron wave are the same.

48. The maximum orbital angular momentum of an electron with $n = 5$ is

$$(1) \sqrt{6} \frac{h}{2\pi} \quad (2) \sqrt{12} \frac{h}{2\pi} \quad (3) \sqrt{42} \frac{h}{2\pi} \quad (4) \sqrt{20} \frac{h}{2\pi}$$

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items in column I with those in column II.

1.

Column I	Column II
a. $\lambda = h/P$	p. UV radiation
b. Lyman series	q. IR radiation
c. Paschen series	r. Pauli's principle
d. $\Delta x \cdot \Delta p \geq h / 4\pi$	s. Heisenberg uncertainty principle
e. Two electrons in any orbital must have an opposite spin	t. de Broglie relationship

2.

Column I	Column II
a. $E = hc\bar{\nu}$	p. Angular momentum of electron in an orbital
b. Orbitals having 2 spherical nodes	q. Aufbau principle
c. $\frac{h}{2\pi} \sqrt{l(l+1)}$	r. Energy of a quantum
d. Occupancy of electrons in degenerate orbitals	s. $3s$ orbitals
e. $4d$ orbitals are filled after $5s$ orbitals	t. Hund's rule

3.

Column I	Column II
a. Discovery of electron	p. Bohr's theory
b. Discovery of neutron	q. Dumb bell
c. Electron revolve around the nucleus in a definite orbit with a definite velocity	r. Balmer
d. Shape of p orbital	s. James Chadwick
e. In hydrogen spectrum transition from n^{th} level to second level correspond to the line.	t. J.J. Thomson

4.

Column I	Column II
a. Plum-Pudding model	p. $1.6022 \times 10^{-19} \text{ C}$
b. Planetary model of atom	q. Thomson's model
c. Atoms are indivisible	r. Rutherford's model
d. Charge on electron	s. $\pm 1/2$
e. The spin of electron is	t. Dalton theory

5.

Column I	Column II
a. The radiation has dual nature.	p. Davisson and Germer
b. The orbital angular momentum of electron in $2s$ orbital is	q. Same atomic number
c. The wave character of electron was experimentally verified by	r. de Broglie
d. Isotopes	s. Zero
e. Isotone	t. Same number of electrons
u. Einstein	


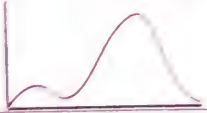
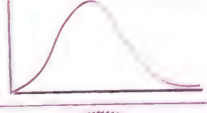

Column I	Column II
a. Orbitals are filled in order of increasing energy	p. Hund's rule
b. Degenerate orbitals are first singly occupied	q. Pauli exclusion principle
c. An orbital can have maximum two electrons	r. Aufbau principle
d. Position and momentum of a small particle cannot be measured simultaneously with absolute accuracy.	s. Heisenberg principle

Column I	Column II
a. Dual character of light	p. Davison
b. Verified dual character of electrons	q. Plank
c. Quantum theory	r. Einstein
d. C has configuration $1s^2 2s^2 2p_x^1$ rather than $1s^2 2p^2 2p_x^1$	s. Pauli

8.

Column I	Column II
a. Configuration of Cr is	p. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
b. Configuration of Cu is	q. 5
c. Number of unpaired electrons in Fe^{3+}	r. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
d. Electronic configuration of Zn^{2+}	s. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
	t. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$
	u. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

9.

Column I	Column II
a. Radial probability distribution graphs for 1s orbital	p. 
b. Radial probability distribution graph for 2s orbital	q. 
c. Radial probability distribution graph for 2p orbitals	r. 
d. Electron cloud picture of 2s orbital	s. 

10.

Column I	Column II
a. Order of screening effect orbitals	p. $4s < 3s < 2s < 1s$
b. Order of energies of orbitals	q. $s > p > d > f$
c. Order of effective nuclear charge in s orbital with different value of n (principal quantum number)	r. $s < p < d < f$
d. Order of energies of visible light	s. Violet > blue > green > yellow > orange > red
	t. Red > orange > yellow > green > blue > violet
	u. $4s > 3s > 2s > 1s$

11.

Column I	Column II
a. $n = 2, l = 1, m = -1$	p. $2p_x$ or $2p_y$
b. $n = 4, l = 2, m = 0$	q. $4s$
c. $n = 3, l = 1, m = \pm 1$	r. $3p_x$ or $3p_y$
d. $n = 4, l = 0, m = 0$	s. $4d_{z^2}$
e. $n = 3, l = 2, m = \pm 2$	t. $3d_{x^2-y^2}$ or $3d_{xy}$

12.

Column I	Column II
a. $2s$	p. $n = 4, l = 2, m = 0$
b. $2p_z$	q. $n = 4, l = 2, m = -2$ or $+2$
c. $4d_{x^2-y^2}$	r. $n = 2, l = 1, m = 0$
d. $4dz^2$	s. $n = 2, l = 0, m = 0$

13.

Column I	Column II
Electronic configuration	Total spin
a. $1s^2$	p. $\pm 5/2$
b. $1s^2 2s^2 2p^6$	q. $\pm 3/2$
c. $1s^2 2s^2 2p^5$	r. $\pm 1/2$
d. $1s^2 2s^2 2p^3$	s. Zero
e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	t. Zero

14.

Column I	Column II
a. $n_1 \rightarrow n_\infty$ in H atoms	p. Visible radiations
b. $n_4 \rightarrow n_2$ in H atoms	q. Energy numerically equal to Rydberg energy
c. $n_\infty \rightarrow n_1$ in He^+ ion	r. Energy numerically equal to ionisation energy
d. $n_4 \rightarrow n_2$ in H atoms	s. Ultraviolet radiations

15.

Column I	Column II
a. Angular momentum	p. Increases by increasing n
b. Kinetic energy	q. Decreases by decreasing Z
c. Potential energy	r. Increases by decreasing Z
d. Velocity	s. Decreases by decreasing n

16.

Column I	Column II
a. Radius of n th orbit	p. Inversely proportional to Z
b. Energy of electron in n th orbit	q. Proportional to n^2
c. Velocity of electron in n th orbit.	r. Inversely proportional to n
d. Angular momentum of electron	s. Proportional to n

17.

Column I	Column II
a. $5 \rightarrow 1$ transition in H atom	p. spectral line in IR region.
b. $7 \rightarrow 1$ transition in H atom	q. spectral line in visible region.
c. Last line of Balmer series in H atom	r. Spectral line in UV region
d. $4 \rightarrow 2$ transition in He^+ ion	s. Spectral line will be observed one.

18.

Column I	Column II
a. Orbit angular momentum	p. $\sqrt{n(n+2)}$
b. Orbital angular momentum	q. $nh/2\pi$
c. Spin angular momentum	r. $\sqrt{s(s+1)} h$
d. Magnetic moment	s. $\sqrt{l(l+1)} h$
	t. $\sqrt{n(n+1)} h$

19.

Column I	Column II
a. Angular momentum	p. Increases by increasing n
b. Kinetic energy	q. Decreases by decreasing Z
c. Potential energy	r. Increases by decreasing Z
d. Velocity	s. Decreases by decreasing n

20.

Column I	Column II
a. $2s$	p. One nodal plane
b. $3p_x$	q. Two nodal planes
c. $4d$	r. Eight nodal planes
d. $3d_{z^2}$	s. Zero nodal plane

21.

Quantum number	Orbitals
a. $n=2, l=1, m=-1$	p. $2p_x$ or $2p_y$
b. $n=4, l=2, m=0$	q. $4d_{z^2}$
c. $n=3, l=1, m=\pm 1$	r. $3p_x$ or $3p_y$
d. $n=4, l=0, m=0$	s. $4s$
e. $n=3, l=2, m=\pm 2$	t. $3dx^2 - y^2$ or $3dxy$

22.

Orbitals	Quantum number
a. $2s$	p. $n=2, l=0, m=0$
b. $2p_z$	q. $n=2, l=1, m=0$
c. $4d_{x^2-y^2}$	q. $n=4, l=2, m=-2$ or $+2$
d. $4d_{z^2}$	r. $n=4, l=2, m=0$

23.

Electronic configuration	Total spin
a. $1s^2$	p. Zero
b. $1s^2 2s^2 2p^6$	q. Zero
c. $1s^2 2s^2 2p^5$	r. $\pm 1/2$
d. $2s^2 2s^2 2p^3$	s. $\pm 3/2$
e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	t. $\pm 5/2$

Numerical Value Type

- What is the total number of pairs of electrons at least same quantum numbers for Be?
(1) 2 (2) 4 (3) 3 (4) 8
- The magnitude of an orbital angular momentum vector of an electron is $\sqrt{6} \frac{h}{2\pi}$. Into how many components will the vector split if an external field is applied to it?
(1) 3 (2) 5 (3) 7 (4) 10
- A certain transition in H spectrum from an excited state to ground state in one or more steps gives rise to total 10 lines. How many of these belong to UV spectrum?
(1) 3 (2) 4 (3) 5 (4) 6
- The uncertainty in the position of an electron is equal to its de Broglie wavelength. The minimum percent error in its measurement of velocity under this circumstance will be approximately.
(1) 4 (2) 8 (3) 18 (4) 22
- The sum of all the quantum numbers of helium atom is.
(1) 1 (2) 2 (3) 3 (4) 4
- The maximum number of electrons that can be accommodated in an orbital is
(1) 1 (2) 3 (3) 2 (4) 4
- The orbital angular momentum quantum number of the state S_2 is
(1) 0 (2) 2 (3) 1 (4) 3
- How many of the following are possible:
 $1p, 2s, 3p, 3f, 3d$
(1) 1 (2) 2 (3) 3 (4) 4
- How many of the following ions have the same magnetic moments?
 $\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Cr}^{2+}, \text{Ni}^{2+}$
(1) 1 (2) 2 (3) 3 (4) 4
- The number of nodes in $3p$ orbital.
(1) 1 (2) 2 (3) 3 (4) 4

11. If each hydrogen atom in the ground state, 1.0 mol of H atoms are excited by absorbing photons of energy

8.4 eV, 12.09 eV, and 15.0 eV of energy, then the number of spectral lines emitted is equal to.

- (1) 1 (2) 2 (3) 3 (4) 4

Archives

JEE MAIN

Single Correct Answer Type

- In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005 %. Certainty with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}$ kg m²/s, mass of electron, $e_m = 9.1 \times 10^{-31}$ kg)

(1) 1.52×10^{-4} m (2) 5.10×10^{-3} m
(3) 1.92×10^{-3} m (4) 3.84×10^{-3} m

(AIEEE 2009)
- Calculate the wavelength (in nanometer) associated with a proton moving at 1×10^3 m/s
(Mass of proton = 1.67×10^{-27} kg and $h = 6.63 \times 10^{-34}$ J.s)

(1) 0.032 nm (2) 0.40 nm
(3) 2.5 nm (4) 14.0 nm

(AIEEE 2009)
- The energy required to break 1 mol of Cl-Cl bonds in Cl₂ is 242 kJ/mol. The longest wavelength of light capable of breaking a single Cl-Cl bond is

(1) 594 nm (2) 640 nm
(3) 700 nm (4) 494 nm

(AIEEE 2010)
- Ionization energy of He⁺ is 19.6×10^{-18} J/atom. The energy of the first stationary state ($n = 1$) of Li²⁺ is

(1) 4.41×10^{-16} J/atom (2) -4.41×10^{-17} J/atom
(3) -2.2×10^{-15} J/atom (4) 8.82×10^{17} J/atom

(AIEEE 2010)
- A gas absorbs photon of 355 nm and emits at two wavelengths. If one of the emission is at 680 nm, the other is at

(1) 1035 nm (2) 325 nm
(3) 743 nm (4) 518 nm

(AIEEE 2011)
- The frequency of light emitted for the transition $n = 4$ to $n = 2$ of He⁺ is equal to the transition in H atom corresponding to which of the following?

(1) $n = 3$ to $n = 1$ (2) $n = 2$ to $n = 1$
(3) $n = 3$ to $n = 2$ (4) $n = 4$ to $n = 3$

(AIEEE 2011)
- The electrons identified by quantum numbers n and l

(1) $n = 4, l = 1$ (2) $n = 4, l = 0$
(3) $n = 3, l = 2$ (4) $n = 3, l = 1$

can be placed in the order of increasing energy as

(1) (3) < (4) < (2) < (1) (2) (4) < (2) < (3) < (1)
(3) (2) < (4) < (1) < (3) (4) (1) < (3) < (2) < (4)

(AIEEE 2012)
- Energy of an electron is given by $E = -2.178 \times 10^{-18}$ J $\left(\frac{Z^2}{n^2}\right)$. Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be ($h = 6.62 \times 10^{-34}$ J.s and $c = 3.0 \times 10^8$ m/s)

(1) 1.214×10^{-7} m (2) 2.816×10^{-7} m
(3) 6.500×10^{-7} m (4) 8.500×10^{-7} m

(JEE Main 2013)

9. The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is

- (1) 5, 0, 0, + $\frac{1}{2}$ (2) 5, 1, 0, + $\frac{1}{2}$
(3) 5, 1, 1, + $\frac{1}{2}$ (4) 5, 0, 1, + $\frac{1}{2}$

(JEE Main 2014)

10. Which of the following is the energy of a possible excited state of hydrogen?

- (1) 13.6 eV (2) -6.8 eV
(3) -3.4 eV (4) +6.8 eV

(JEE Main 2015)

11. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron respectively, then the value of h/λ (where λ is wavelength associated with electron wave) is given by:

(JEE Main 2016)

- (1) $\sqrt{2meV}$ (2) meV
(3) $2 meV$ (4) \sqrt{meV}

12. The radius of the second Bohr orbit for hydrogen atom is:

(Planck's Const. $h = 6.6262 \times 10^{-34}$ Js;
mass of electron = 9.1091×10^{-31} kg;
charge of electron $e = 1.60210 \times 10^{-19}$ C;
permittivity of vacuum

- $e_0 = 8.854185 \times 10^{-12}$ kg⁻¹ m⁻³ A²)
(1) 1.65 Å (2) 4.76 Å
(3) 0.529 Å (4) 2.12 Å

(JEE Main 2017)

JEE ADVANCED

Single Correct Answer Type

- Given that the abundance of the isotopes ⁵⁴Fe, ⁵⁶Fe, and ⁵⁷Fe are 5%, 90%, and 5%, respectively, the atomic mass of Fe is

(1) 55.85 (2) 55.95 (3) 55.75 (4) 55.05

(IIT-JEE 2009)
- The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius]

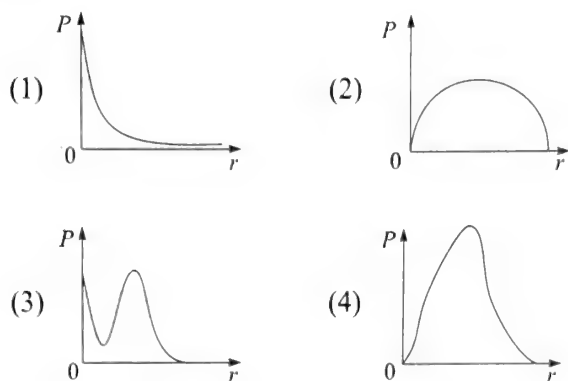
(1) $\frac{h^2}{4\pi^2 ma_0^2}$ (2) $\frac{h^2}{16\pi^2 ma_0^2}$
(3) $\frac{h^2}{32\pi^2 ma_0^2}$ (4) $\frac{h^2}{64\pi^2 ma_0^2}$

(IIT-JEE 2012)

3. The first ionization potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^\oplus will be :

- (1) -5.1 eV (2) -10.2 eV
(3) +2.55 eV (4) -2.55 eV (JEE Advanced 2013)

4. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr , at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is



(JEE Advanced 2016)

Linked Comprehension Type

Paragraph 1

The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light, the ion undergoes transition to a state S_2 . The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

(IIT-JEE 2010)

1. The state S_1 is

- (1) 1s (2) 2s
(3) 2p (4) 3s

2. Energy of the state S_1 in units of the hydrogen atom ground state energy is

- (1) 0.75 (2) 1.50
(3) 2.25 (4) 4.50

3. The orbital angular momentum quantum number of the state S_2 is

- (1) 0 (2) 1
(3) 2 (4) 3

Matrix Match Type

Answer Q. 1, Q. 2 and Q. 3 by appropriately matching the information given in the three columns of the following table.

The Wave function Ψ_{n, l, m_l} is a mathematical function whose value depends upon spherical polar coordinates (r, θ, ϕ) of the electron and characterized by the quantum numbers n, l and m_l . Here r is distance from nucleus, θ is colatitude and ϕ is azimuth. In the mathematical functions given in the Table, Z is atomic number and a_0 is atomic number and a_0 is Bohr radius.

Column I	Column II	Column III
(I) 1s orbital	(i) $\Psi_{n, l, m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\left(\frac{Zr}{a_0}\right)}$	(P)
(II) 2s orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto \frac{1}{a_0^3}$
(III) 2p _z orbital	(iii) $\Psi_{n, l, m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\left(\frac{Zr}{2a_0}\right)} \cos \theta$	(R) Probability density is maximum at nucleus
(IV) 3d _{xy} orbital	(iv) xy-plane is a nodal plane	(S) Energy needed to excite electron from $n = 2$ state to $n = 4$ state is $\frac{27}{32}$ times the energy needed to excite electron from $n = 2$ state to $n = 6$ state

(JEE Advanced 2017)

1. For the given orbital in Column 1, the only CORRECT combination for any hydrogen-like species is

- (1) (IV) (iv) (R) (2) (II) (ii) (P)
(3) (III) (iii) (P) (4) (I) (ii) (S)

2. For He^\oplus ion, the only INCORRECT combination is

- (1) (II) (ii) (Q) (2) (I) (i) (S)
(3) (I) (i) (R) (4) (I) (iii) (R)

3. For hydrogen atom, the only CORRECT combination is

- (1) (I) (iv) (R) (2) (I) (i) (P)
(3) (II) (i) (Q) (4) (I) (i) (S)

Numerical Value Type

1. The maximum number of electrons can have principal quantum number $n = 3$ and spin quantum number $m_s = -1/2$ is

(IIT-JEE 2011)

2. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

(IIT-JEE 2011)

3. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at -73°C is "M" times that of the de Broglie wavelength of Ne at 727°C . M is (JEE Advanced 2013)

4. In an atom, the total number of electrons having quantum numbers $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is (JEE Advanced 2014)
5. Not considering the electronic spin, the degeneracy of the second excited state ($n = 3$) of H atom is 9, while the degeneracy of the second excited state of H^{\oplus} is (JEE Advanced 2015)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|----------|----------|-----------|----------|----------|
| 1. (3) | 2. (4) | 3. (1) | 4. (3) | 5. (3) |
| 6. (1) | 7. (3) | 8. (1) | 9. (4) | 10. (1) |
| 11. (4) | 12. (4) | 13. (4) | 14. (3) | 15. (4) |
| 16. (3) | 17. (2) | 18. (3) | 19. (1) | 20. (2) |
| 21. (4) | 22. (2) | 23. (1) | 24. (1) | 25. (3) |
| 26. (3) | 27. (2) | 28. (3) | 29. (3) | 30. (4) |
| 31. (4) | 32. (4) | 33. (3) | 34. (2) | 35. (3) |
| 36. (1) | 37. (3) | 38. (2) | 39. (3) | 40. (1) |
| 41. (3) | 42. (1) | 43. (3) | 44. (4) | 45. (3) |
| 46. (2) | 47. (3) | 48. (2) | 49. (3) | 50. (3) |
| 51. (4) | 52. (4) | 53. (1) | 54. (1) | 55. (1) |
| 56. (1) | 57. (1) | 58. (1) | 59. (2) | 60. d |
| 61. (3) | 62. (1) | 63. (1) | 64. (2) | 65. (3) |
| 66. (4) | 67. (3) | 68. (3) | 69. (1) | 70. (2) |
| 71. (2) | 72. (4)b | 73. (1) | 74. (1) | 75. (3) |
| 76. (1) | 77. (1) | 78. (3) | 79. (1) | 80. (1) |
| 81. (2) | 82. (1) | 83. (1) | 84. (2) | 85. (1) |
| 86. (3) | 87. (4) | 88. (3) | 89. (1) | 90. (2) |
| 91. (4) | 92. (2) | 93. (4) | 94. (1) | 95. (1) |
| 96. (1) | 97. (1) | 98. (1) | 99. (4) | 100. (1) |
| 101. (3) | 102. (1) | 103. a, d | 104. (2) | 105. (3) |
| 106. (4) | 107. (2) | 108. (1) | 109. (3) | 110. (2) |
| 111. (1) | 112. (1) | 113. (4) | 114. (4) | 115. (2) |
| 116. (3) | 117. (3) | 118. (2) | 119. (2) | 120. b |
| 121. (1) | 122. (2) | 123. (3) | 124. (3) | 125. d |
| 126. (4) | 127. (2) | 128. (4) | | |

Multiple Correct Answers Type

- | | | |
|--------------|-----------------|---------------|
| 1. (1, 2, 3) | 2. (1, 4) | 3. (2, 4) |
| 4. (2, 4) | 5. (2, 3) | 6. (2, 3) |
| 7. (1, 2, 3) | 8. (1, 2, 3, 4) | 9. (1, 2, 3) |
| 10. (1) | 11. (1, 3) | 12. (1, 2, 3) |
| 13. (1, 4) | 14. (1) | 15. (1, 2) |
| 16. (1, 2) | 17. (2, 3) | 18. (2, 4) |
| 19. (4) | 20. (1, 2, 4) | 21. (2, 3, 4) |
| 22. (2) | 23. (2, 3, 4) | 24. (1, 2) |
| 25. (3) | 26. (1, 2, 3) | 27. (1, 2) |

- | | | |
|---------------|------------------|------------------|
| 28. (3) | 29. (2) | 30. (1) |
| 31. (3) | 32. (1, 2, 3) | 33. (1, 2, 4) |
| 34. (2, 3, 4) | 35. (1, 2, 3) | 36. (1, 2) |
| 37. (2, 3) | 38. (2, 4) | 39. (1, 2) |
| 40. (1, 2, 3) | 41. (1, 2, 3) | 42. (1, 2, 3) |
| 43. (1, 2, 3) | 44. (1, 2, 3, 4) | 45. (1, 2, 3, 4) |

Linked Comprehension Type

- | | | | | |
|---------|---------|---------|---------|---------------|
| 1. (1) | 2. (2) | 3. (4) | 4. (2) | 5. (4) |
| 6. (3) | 7. (1) | 8. (2) | 9. (2) | 10. (3) |
| 11. (3) | 12. (3) | 13. (1) | 14. (3) | 15. (1, 2, 4) |
| 16. (2) | 17. (2) | 18. (4) | 19. (1) | 20. (4) |
| 21. (2) | 22. (1) | 23. (1) | 24. (4) | 25. (1) |
| 26. (1) | 27. (2) | 28. (2) | 29. (3) | 30. (1) |
| 31. (1) | 32. (1) | 33. (1) | 34. (1) | 35. (1) |
| 36. (3) | 37. (4) | 38. (4) | 39. (1) | 40. (3) |
| 41. (1) | 42. (4) | 43. (2) | 44. (3) | 45. (4) |
| 46. (3) | 47. (1) | 48. (4) | | |

Matrix Match Type

	a	b	c	d	e
1.	t	p	s	r	—
2.	r	s	p	t	q
3.	t	s	p	q	r
4.	q	r	r	p	s
5.	u	s	p	q	t
6.	r	p	q	s	—
7.	r	p	q	s	—
8.	r	s	q	p	—
9.	p	q	r	s	—
10.	q	r	p	s	—
11.	p	s	r	q	t
12.	s	r	q	p	—

13.	t	s	r	q	p
14.	q, r, s	s	r, s	p	—
15.	p, s	q	p, r, s	q	—
16.	p, q	q	r	s	—
17.	r, s	p, q	r, s	r, s	—
18.	q	s	r	p	—
19.	p	q	r	s	t
20.	f	q	r	s	—
21.	p	q	r	s	t
22.	p	q	r	s	—
23.	p	q	r	s	t

Numerical Value Type

1. (2) 2. (2) 3. (2) 4. (2) 5. (1)
 6. (3) 7. (3) 8. (3) 9. (2) 10. (1)
 11. (3)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (3) 2. (2) 3. (4) 4. (2) 5. (3)
 6. (2) 7. (2) 8. (1) 9. (1) 10. (2)
 11. (1) 12. (4)

JEE Advanced**Single Correct Answer Type**

1. (2) 2. (2) 3. (2) 4. (4)

Linked Comprehension Type

1. (2) 2. (3) 3. (2)

Matrix Match Type

1. (1) 2. (3) 3. (4)

Numerical Value Type

1. (9) 2. (4) 3. (5) 4. (6) 5. (3)

OVERVIEW

- The constituent particles (atoms or molecules) of a solid do not have translatory or rotatory motion, but they possess vibratory motion.
- The energies of the three states of matter are in the following order:

$$\text{Solids} < \text{Liquids} < \text{Gases}$$

- $1 \text{ atm} = 76 \text{ cm} = 760 \text{ mm} = 760 \text{ torr}$
 $= 101325 \text{ Pa or N m}^{-2} = 1.01325 \times 10^5 \text{ Pa or N m}^{-2}$
 $= 10^5 \text{ Pa or N m}^{-2}$

$$1 \text{ atm} = 1.013 \text{ bar}$$

$$1 \text{ bar} = 0.987 \text{ atm} = 10^2 \text{ K Pa}$$

$$1 \text{ atm} = 0.06805 \text{ psi}$$

$$1 \text{ N m}^{-2} = 6894.8 \text{ psi}$$

Pascal is defined as pressure exerted when a force of 1 Newton (1 N) acts on an area 1 m^2 .

Newton is a force that gives a mass of 1 kg and an acceleration of 1 ms^{-2} . ($1 \text{ N} = 1 \text{ kg ms}^{-2}$)

- $^{\circ}\text{C} = t + 273.15 \text{ K}$, $0^{\circ}\text{C} = 273.15 \text{ K}$

- $^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32)$ and $^{\circ}\text{F} = \frac{9}{5} (^{\circ}\text{C}) + 32$

b. Beckmann thermometer: It cannot be used to measure temperature. It is used only for the measurement of small difference of temperatures.

c. The barometric formula: It is found that as we go higher up the sea level, the pressure of atmosphere decreases. The variation of pressure with altitude is given by barometric formula. If P_0 is the pressure at sea level, T is the temperature on kelvin scale, the pressure P at a height of x m above sea level is

$$\ln\left(\frac{P}{P_0}\right) = \frac{M_m g x}{RT}$$

Here, M_m is average molecular mass of air ($29 \times 10^{-3} \text{ kg mol}^{-1}$); g is acceleration due to gravity (9.8 m s^{-2}) and R is gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

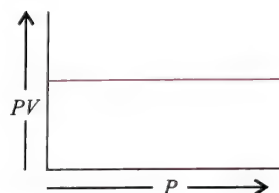
- Boyle's law:** The volume of a definite mass of gas is inversely proportional to its pressure at constant temperature.

$$P_1 V_1 = P_2 V_2 \text{ at constant temperature.}$$

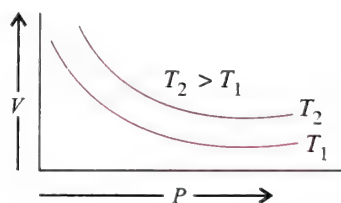
- The plot of P vs $1/V$ at constant T is a straight line passing through the origin.



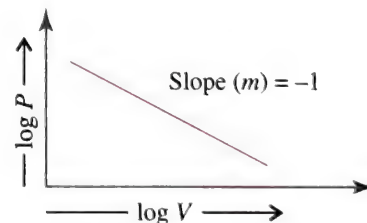
- The plot of PV vs P is a straight line parallel to the X-axis.



- The plot of V vs P is a hyperbola.



-



- The density of a gas is directly proportional to its pressure. At high altitudes, as pressure is low, the density of air is less. That is why mountaineers carry oxygen cylinders.
- Charles' law:** The volume of a definite mass of gas is directly proportional to its temperature (in kelvin) at constant pressure.

At constant pressure, volume at $t^{\circ}\text{C}$,

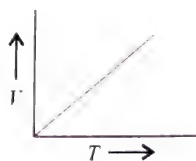
$$V_t = V_0 + \frac{V_0}{273} \times t = V_0 \left(\frac{273 + t}{273} \right) = V_0 \frac{T}{273}$$

$$\text{i.e., } V_1 \propto T$$

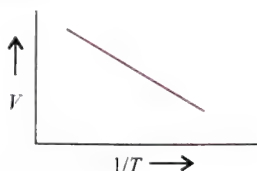
$$\text{or } \frac{V}{T} = \text{constant}$$

$$\text{i.e., } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

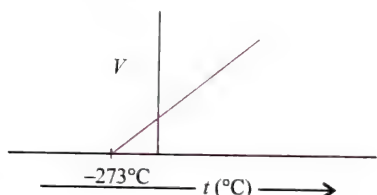
a. Plot of V vs T



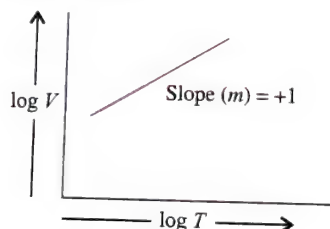
b. Plot of V vs $1/T$



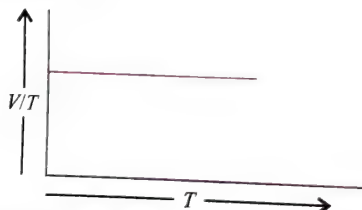
c. Plot of V vs t ($^{\circ}\text{C}$)



d. Plot of $\log V$ vs $\log T$



e. Plot of V/T vs T



10. According to P - T law or *Amonton's law*, or Gay Lussac's law at constant volume, pressure at $t^{\circ}\text{C}$:

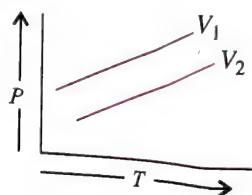
$$P_t = P_0 \left(1 + \frac{t}{273} \right) = P_0 \frac{273+t}{273} = P_0 \frac{T}{273}$$

$$\text{i.e., } P_t \propto T$$

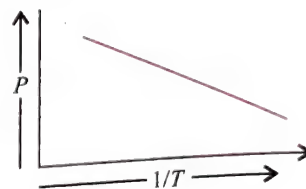
$$\text{or } \frac{P}{T} = \text{constant}$$

$$\text{i.e., } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

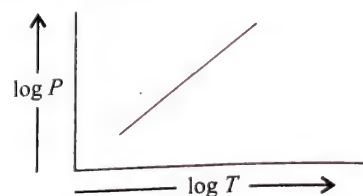
a. Plot of P vs T



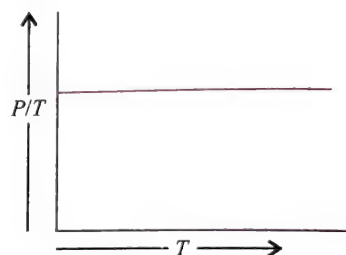
b. Plot of P vs $1/T$



c. Plot of $\log P$ vs $\log T$



d. Plot of P/T vs T



e. The plots drawn at constant temperature for a gas are called **Isotherms**.

f. The plots drawn at constant pressure for a gas are called **Isobars**.

g. The plot drawn at constant volume for a gas is called as **Isochore**.

h. **Volume coefficient (α_v)**: It is a ratio of increase in volume of a gas at constant pressure per degree rise in temperature of its volume at 0°C

$$\alpha_v = \frac{P_f - V_o}{V_o \times t}$$

$$\text{(the value of } \alpha_v = \frac{1}{273} \text{ for all gases)}$$

i. **Pressure coefficient (α_p)**: It is the ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C .

$$\alpha_p = \frac{P_f - P_o}{P_o \times t}$$

$$\text{(the value of } \alpha_p = \frac{1}{273} \text{ for all gases)}$$

11. **Density and molar mass of a gas**: According to the ideal gas equation $PV = nRT$,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Expressing in terms of density, we get

$$P = \frac{m}{M_w} \frac{RT}{V} = \frac{m}{V} \frac{RT}{M_w} = d \frac{RT}{M_w}$$

$$\text{or } M_w = d \frac{RT}{P}$$

12. a. STP (Standard temperature and pressure) or NTP (normal temperature and pressure) conditions are $T = 0^\circ\text{C} = 273.15\text{ K}$, $P = 1\text{ atm}$
- or
- $$T = 0^\circ\text{C} = 273.15\text{ K}, \quad P = 1\text{ bar}$$
- i. Volume of a gas at STP ($P = 1\text{ atm}$)
- $$= 22.413996\text{ L mol}^{-1} \approx 22.4\text{ L mol}^{-1}$$
- ii. Volume of a gas at STP ($P = 1\text{ bar}$)
- $$= 22.71098\text{ L mol}^{-1} \approx 22.7\text{ L mol}^{-1}$$
- b. SATP (standard ambient temperature and pressure) or standard conditions are:
- i. $T = 25^\circ\text{C} = 298.15\text{ K}$, $P = 1\text{ atm}$
- or
- ii. $T = 25^\circ\text{C} = 298.15\text{ K}$, $P = 1\text{ bar}$ (10^5 Pa)
- iii. Volume of a gas at SATP (or standard conditions) when ($P = 1\text{ atm}$) = 24.4 L mol^{-1} .
- iv. Volume of a gas at SATP (or standard conditions) when ($P = 1\text{ bar}$) = 24.789 L mol^{-1}
- $$= 24.7\text{ L mol}^{-1}$$
- c. Volume of a gas is expressed is m^3 or cm^3 or mL or litres or dm^3
- $$1\text{ L} = 10^3\text{ cm}^3 = 10^{-3}\text{ m}^3 = 1\text{ dm}^3$$
13. a. Gas constant R , is work done per degree per mole. Its value is
- $$0.0821\text{ L atm deg}^{-1}\text{ mol}^{-1}$$
- or $82.1\text{ cm}^3\text{ atm deg}^{-1}\text{ mol}^{-1}$
- or $8.314 \times 10^7\text{ erg deg}^{-1}\text{ mol}^{-1}$
- or $8.3\text{ m Nm K}^{-1}\text{ mol}^{-1}$ (S.I. units)
- or $8.314\text{ J K}^{-1}\text{ mol}^{-1}$ or $\text{kPa dm}^3\text{ K}^{-1}\text{ mol}^{-1}$ (S.I. units)
- or $8.314\text{ MPa cm}^3\text{ K}^{-1}\text{ mol}^{-1}$
- or $1.987\text{ cal deg}^{-1}\text{ mol}^{-1}$
- b. The value of R can also be given in electron volts per degree per mol.
- 1 eV is the energy acquired by electron in passing through a potential difference of one volt.
- $$1\text{ eV} = 1.602 \times 10^{-19}\text{ volts coulomb (Joule)}$$
- $$R = (8.314\text{ JK}^{-1}\text{ mol}^{-1}) \left(\frac{1}{1.602 \times 10^{-19}}\text{ eV J}^{-1} \right)$$
- $$= 5.189 \times 10^{19}\text{ eV K}^{-1}\text{ mol}^{-1}$$
- c. **Avogadro's law:** Equal volume of all gases under similar conditions of T and P contains equal number of molecules i.e.,
- $$V \propto N \quad \text{or} \quad V \propto n \quad (\text{at constant } T, P)$$
14. a. According to **Dalton's law** of partial pressures, for a number of non-reacting gases mixed together,
- $$P_{\text{total}} = p_1 + p_2 + p_3 + \dots \quad (\text{i.e., total pressure is the sum of partial pressures of the gases}).$$
- b. In a mixture of gases, the partial pressure of any gas A = Mole fraction of A \times Total pressure.
- c. **Atomolysis:** The process of separation of gases from their gaseous mixture by using the principle of diffusion is known as **Atomolysis**.
15. a. **Aqueous tension:** When a gas is collected over water by downward displacement of water, it becomes moist due to water vapours present in it which it carries with it while passing through water. These water vapours also exert their own pressure at the temperature of the gas. The **partial pressure of the water vapours at a particular temperature is known as aqueous tension at that temperature.**
- Vapour pressure of dry gas
- $$= \left[\text{Vapour pressure of wet gas} \right] - \left[\text{Vapour pressure of water vapour (aqueous tension)} \right]$$
- b. **Relative humidity (R.H.)** at a given temperature
- $$= \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$
- c. **Amagat's law of partial volume:** It states that total volume of mixture of gases which do not react at constant temperature is equal to the sum of the individual partial volumes of the constituents.
- $$V = v_1 + v_2 + v_3 + \dots + v_n$$
- $$= \sum v_i$$
- d. **Pay load of a balloon** = (Mass of displaced air – mass of balloon)
- e. **Triple point:** At 4.7 mm Hg pressure and at 0.0098°C , ice (solid), water (liquid) and vapour (gas) may coexist simultaneously and all are stable.
- $$\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour}$$
- The corresponding temperature at which all the three states coexist is called **triple point**.
- f. Pressure of a gas is measured by **manometer** while atmospheric pressure is measured on **Barometer**.
16. According to **Graham's law of diffusion**, under similar conditions of temperature and pressure, if r_1 and r_2 are the rates of diffusion of two gases with densities d_1 and d_2 , then
- $$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{Mw_2}{Mw_1}}$$
- For gases at different pressures, $\left(r \propto \frac{P}{\sqrt{Mw}} \right)$
- $$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{Mw_2}{Mw_1}}$$
- For gases at different temperatures, $\left(r \propto \sqrt{\frac{T}{Mw}} \right)$
- $$\frac{r_1}{r_2} = \sqrt{\frac{T_1 Mw_2}{T_2 Mw_1}}$$
17. The volume occupied by a gas under normal conditions of temperature and pressure is mainly due to empty spaces present between the molecules.
18. The average kinetic energy of a gas is directly proportional to its absolute temperature.
19. Most probable velocity (α) increases with an increase in temperature, but the fraction of molecules possessing this velocity decreases with an increase in temperature.

20. According to kinetic gas equation, $PV = \frac{1}{3} mnu^2$ (where m is the mass of each molecule, n is the number of molecules, and u is the RMS velocity).

21. Most probable velocity, $\alpha = \sqrt{\frac{2RT}{M_w}}$

Average velocity, $v = \sqrt{\frac{8RT}{\pi M_w}}$

RMS velocity, $u = \sqrt{\frac{3PV}{M_w}} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3P}{d}}$
(d = density of the gas)

22. $\alpha(\text{MPV}) : v(\text{AV}) : u(\text{RMS}) = 1 : 1.128 : 1.224$

$v(\text{RMS}) : v(\text{AV}) : \alpha(\text{MPV}) = 1 : 0.921 : 0.816$

23. a. Average KE of a gas,

$$KE = \frac{3}{2} kT \quad (k = \text{Boltzmann constant})$$

- b. Gas constant per molecule is known as **Boltzmann constant (k)**.

$$k = \frac{R}{N_A} = \frac{8.314 \text{ JK}^{-1}}{6.022 \times 10^{23} \text{ molecules}} = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}$$

24. **Compressibility factor**, $Z = \frac{PV}{nRT}$

25. For an ideal gas, $Z = 1$. For a real gas, $Z \neq 1$.

26. If $Z < 1$, a gas shows negative deviation, i.e., it is more compressible than expected from ideal behaviour. If $Z > 1$, the gas shows positive deviation.

27. For most gases, $Z < 1$ at low pressure which increases with pressure and becomes greater than 1. For H_2 and He, Z is always greater than 1. This is because of their small size, which makes intermolecular forces of attraction negligible.

28. As temperature increases, deviation from ideal behaviour decreases. The temperature at which a real gas behaves like an ideal gas is called '**Boyle temperature**'.

$$T_B(\text{Boyle temperature}) = \frac{a}{Rb}$$

29. Gases behave like ideal gases only at high temperature and low pressure.

30. The equation of state for real gases (called **van der Waals equation**) is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

for 1 mol of the gas.

For n moles of the gas, the equation is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

31. The **van der Waals constant** a is a measure of the magnitude of the attractive forces among the molecules of the gas. The greater the value of a , the larger the intermolecular forces of attraction.

32. The **van der Waals constant** b is a measure of the effective size of the gas molecules. Its value is equal to four times the

actual volume of the gas molecules. It is called **excluded volume** or **co-volume**.

$b = 4 \times \text{Volume occupied by the molecules in 1 mol of a gas.}$

$$b = 4 \left(\frac{4}{3} \pi r^3\right) N_A = 4 \times \frac{4}{3} \times 3.14 \times r^3 \times 6 \times 10^{23} \\ \approx 96 \times 10^{23} r^3 \text{ mL mol}^{-1}$$

Use direct formula:

$$b \approx 96 \times 10^{23} \times r^3 \times (10^{-8})^3 \text{ mL mol}^{-1} \text{ (If } r \text{ is given in } \text{\AA})$$

33. Unit of a is $\text{atm L}^2 \text{ mol}^{-1}$, and unit of b is L mol^{-1} .

34. A gas can be liquefied by cooling or by applying pressure or by the combined effect of both. However, the effect of temperature is more important because for every gas there is a particular temperature above which it cannot be liquefied howsoever high pressure is applied. This temperature is called **critical temperature**. A gas can be liquefied if its temperature is below

$$T_c = \frac{8a}{27Rb} \text{ its critical temperature}$$

35. The critical temperature of a gas is a measure of the strength of intermolecular forces of attraction in that gas. The weaker the intermolecular forces, the greater the difficulty in liquefying and hence the lower the critical temperature. The van der Waals constant a increases in the same order as critical temperature.

36. **Joule-Thomson effect** states that 'when a real gas is allowed to expand adiabatically through a fine hole from a region of high pressure to a region of low pressure, it is accompanied by cooling (except H_2 and He which show heating effect).'

37. **Critical pressure (P_c)** is the minimum pressure required to liquefy a gas. Its relation with van der Waals constants is given below:

$$P_c = \frac{a}{27b^2}$$

38. **Critical volume (V_c)** is the volume occupied by a gas at critical temperature and critical pressure. It is given as:

$$V_c = 3b$$

39. **Critical compressibility factor:**

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

40. a. **Critical constants in terms of van der Waals constants.**

The critical constants are related to van der Waals constants by the following expressions

$$T_c = \frac{8a}{27Rb}, T_c = \frac{8a}{27Rb}, V_c = 3b$$

They are related to each other as

$$P_c V_c = \frac{3}{8} RT_c$$

- b. **Boyle temperature (T_B) and critical temperature (T_c) in terms of van der Waals constants:**

$$T_B = \frac{a}{Rb}, T_c = \frac{8a}{27Rb}$$

$$\text{Thus, } T_B > T_c$$

41. **a. Inversion temperature (T_i):** Every gas has a definite temperature at which it shows neither heating effect nor cooling effect when allowed to expand adiabatically according to Joule–Thomson effect. Above this temperature, the gas shows heating effect, and below this temperature, it shows cooling effect. This temperature is called inversion temperature. Most of the gases have high inversion temperatures (much higher than the room temperature). Hydrogen and helium have low inversion temperatures.

$$\text{b. } T_c < T_B < T_i \left(\frac{8a}{27Rb} < \frac{a}{Rb} < \frac{2a}{Rb} \right) = 8 : 27 : 54$$

42. **Kinetic theory of gases:**

Dynamic Particle Model or Microscopic Model of a Gas: To explain the properties of gases this theory was put forward by **D. Bernauli** and developed by **Clausius, Boltzmann, Kelvin** etc. It was known as **kinetic molecular theory of gases** as it assumes the gas to be made of a large number of molecules in ceaseless motion. For the same reason it is also called a **Dynamic particle model**. The name **microscopic model** is also used as it assumes the gas to be made up of molecules which cannot be seen.

a. Assumptions of kinetic theory of gases

- Every gas is made up of a large number of minute particles called molecules. All the molecules of a particular gas are identical in mass and size and differ in these from gas to gas.
- The molecules are so small and are separated from each other by large distances so that their actual volume is negligible as compared to the total volume of the gas.
- The molecules of a gas are not stationary but are moving continuously very fast in all directions in a straight line until their directions in motion are changed on collision with one another or with the walls of the container.
- There are no attractive forces between the molecules. The force of gravity on them is also negligible.
- The molecules are spherical and perfectly elastic. Therefore, there is no loss of kinetic energy due to collision or mutual friction.
- The pressure exerted by a gas is due to the bombardment of the moving molecules against the walls of the container.
- Since different molecules in a gas move with different velocities, they have different kinetic energies. However average kinetic energy of the molecules is proportional to absolute temperature of the gas.

43. **Kinetic gas equation:** Based on assumption of kinetic theory, the following mathematical expression is derived for **any ideal gas**.

$$PV = \frac{1}{3} mNu^2$$

Here, P = pressure of gas, V = volume of gas, m = mass of each molecule, N = Total number of molecules, u = r.m.s. velocity.

For 1 mole of gas $m \times N$ = Molecular (M_w) mass
Therefore the above equation can be written as

$$PV = \frac{1}{3} Mwu^2$$

From the above equation the root mean square velocity of the gas can be calculated.

$$u = \sqrt{\frac{3PV}{Mw}} \quad \text{or} \quad \sqrt{\frac{3RT}{Mw}} \quad \text{or} \quad \sqrt{\frac{3P}{d}}$$

When $R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$, then

$$u = \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{Mw}} \\ = 1.58 \sqrt{\left(\frac{T}{Mw}\right)} \times 10^4 \text{ cm s}^{-1}$$

44. **Calculation of kinetic energy**

According to gas equation,

$$PV = \frac{1}{3} Mwu^2 \text{ for 1 mole of gas}$$

$$\text{or} \quad PV = \frac{2}{3} \times \frac{1}{2} Mwu^2$$

$$\text{or} \quad \frac{1}{2} Mwu^2 = \frac{3}{2} PV = \frac{3}{2} RT$$

$$\text{So} \quad \text{K.E.} = \frac{3}{2}$$

$$\text{For 1 molecule the K.E.} = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} kT$$

$$\left\{ \frac{R}{N_A} = k \text{ (Boltzmann constant)} \right\}$$

- Kinetic energy of a gas is directly proportional to its absolute temperature. This is known as **Maxwell's generalisation**.
- The average kinetic energy of gas molecule is independent of the mass of the gas molecules.
- At absolute zero, the kinetic energy of gas molecule becomes zero.
- According to kinetic theory of gases for 1 mole of gas, **Boyle's law** is expressed as

$$PV = \frac{1}{3} Mwu^2$$

where M is molecular mass of the gas and u = RMS velocity

- According to kinetic theory of gases for 1 mole of gas, **Charle's law** is expressed as

$$V = \left(\frac{Mw}{3P} \right) u^2$$

- f. According to kinetic theory of gases for 1 mole of gas, **Amonton's law** is expressed as

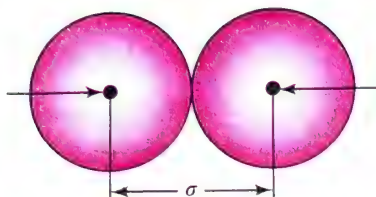
$$P = \left(\frac{Mw}{3V} \right) u^2$$

- g. Kinetic energy of 1 mole of gas = $\frac{1}{2} m N_A u^2$

N_A = Avogadro's number.

Molecular Collisions:

45. **Collision diameter (σ):** When two molecules of a gas come close to each other, a stage comes when the repulsion starts acting between them. The equilibrium distance between the centres of the molecules when they are closest to each other (i.e., just before the repulsion starts) is called collision diameter.



46. **Collision number (N_C):** The number of collision which a single molecule undergoes with other molecules in one second is called **collision number**.

$$N_C = \sqrt{2} \pi \bar{v} \sigma^2 N/V$$

where \bar{v} = average velocity

σ = molecular diameter

N/V = number of molecules of gas per cm^3

47. **Collision frequency (Z):** The total number of collisions which take place in one second amongst the molecules present in 1 cm^3 of the gas is called **collision frequency**.

Mathematically, Z = No. of collisions of single molecule (N_C) \times No. of molecules in 1 cm^3 (N/V)

As a binary collision involves two molecules.

\therefore Collision frequency,

$$Z = \frac{N_C \times N/V}{2} = \frac{\sqrt{2} \pi \bar{v} \sigma^2 N/V \times N/V}{2}$$

$$= \frac{\pi \bar{v} \sigma^2 (N/V)^2}{\sqrt{2}}$$

Putting $\bar{v} = \sqrt{\frac{8RT}{\pi Mw}}$

$$Z = \frac{\pi \sigma^2 (N/V)^2}{\sqrt{2}} \sqrt{\frac{8RT}{\pi Mw}} = 2\sigma^2 (N/V)^2 \sqrt{\frac{\pi RT}{Mw}}$$

- On increasing temperature (T) average velocity (\bar{v}) increases.
- On increasing pressure (P) number of molecules per cm^3 of gas, (n) increases.
- On increasing \bar{v} or n , collision frequency (Z) increases. Therefore, Z increases on increasing T or P .

i. At a particular temperature $Z \propto P^2$

ii. At a particular pressure $Z \propto T^{-3/2}$

iii. At a particular volume $Z \propto T^{1/2}$

48. **Mean free path (λ):** The distance travelled by a molecule between any two successive collisions is called free path. The average of these distances ($d_1, d_2, d_3, \dots, d_n$) is called mean free path λ .

Thus, mean free path,

$$\lambda = \frac{\text{Average distance travelled by molecule } (\bar{v})}{\text{No. of collisions } (N_C)}$$

$$\text{Mathematically, } \lambda = \frac{\bar{v}}{N_C} = \frac{1}{\sqrt{2} \pi \sigma^2 N/V}$$

where σ = collision diameter and N/V is the number of molecules of the gas per unit volume. For n moles of the gas $PV = nRT$ or $PV = N/N_A RT$.

\therefore Number of molecules per unit volume,

$$N/V = \frac{P \cdot N_A}{RT}$$

where N_A = Avogadro's number

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2} \frac{RT}{PN_A}$$

Thus $\lambda = \frac{T}{P}$

- At a constant pressure the mean free path increases with increase in temperature and vice-versa.
- At a constant temperature, the mean free path increases with the decrease in pressure and vice-versa.
- At constant temperature and pressure, lesser the collision diameter, σ , more is the mean free path, λ .

49. **Molar heat capacity:** It is amount of heat required to raise the temperature of 1 mole of a **substance through 1°C**

Molar heat = Specific heat \times Molar mass

(Specific heat is amount of heat required to raise the temperature of 1g of a substance through 1°C) Heat capacity at constant volume = C_v , and at constant pressure = C_p .

Some useful relations of C_p and C_v are

i. $C_p - C_v = R = 2 \text{ cal} = 8.314 \text{ J}$

ii. $\frac{C_p}{C_v} = \frac{3}{2} R$

iii. $\frac{C_p}{C_v} = \gamma$

iv. For monoatomic gas, $C_v = 3 \text{ calories}$

v. For monoatomic gases, $\frac{C_p}{C_v} = \frac{5}{3} = 1.66$

vi. For diatomic gases, $\frac{C_p}{C_v} = 1.40$

$$\left(C_v = \frac{5}{3} R, C_p = \frac{7}{2} R \right)$$

vii. For triatomic gases, $\frac{C_p}{C_v} = 1.33$ ($C_v = 6R$, $C_p = 8R$)

50. Average molecular weight of a gaseous mixture

$M_{\text{mix}} = \frac{\sum n_i M_i}{\sum n_i}$, where n_i is the number of moles and M_i is the molecular weight of the component.

51. Liquid state: This state is intermediate between solid state and gaseous state as regards to interparticle forces, packing of particles, etc. Some characteristic properties of the liquids are:

a. **Evaporation:** It is the spontaneous change in which a liquid changes into the vapours at the surface of the liquid. Evaporation occurs at all temperatures. Evaporation increases with increase in surface area, increase in temperature and decrease in intermolecular attractive forces. In contrast to evaporation boiling takes place only at definite temperature and it **involves bubble formation below the surface**. Evaporation causes cooling.

b. **Vapour pressure:** It is the pressure exerted by the vapours of the liquid in equilibrium with its liquid at a given temperature. Vapour pressure of a liquid increase with increase in temperature. Liquids having weak intermolecular attractive forces have a high tendency to evaporate and, therefore, have high vapour pressure.

c. **Boiling point:** The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure is called **boiling point**. Boiling point of a liquid increases with increase in external pressure. Liquids having weak attractive forces have low boiling points and vice versa. The temperature of a boiling liquid always remains constant.

d. **Surface tension:** The force that acts at right angles to an imaginary line on unit length at the surface of the liquid at rest. It is expressed in J m^{-2} or N m^{-1} . Surface tension of a liquid generally decreases with increase in temperature. It is measured by an apparatus called **stalagmometer**

e. **Coefficient of viscosity:** The force in newtons per square meter required to maintain a difference of viscosity of one meter per second, between two parallel layers of the liquid at a distance of one meter from each other. It is expressed in $\text{kg m}^{-1} \text{s}^{-1}$. Liquids having stronger attractive forces are more viscous.

The force of attraction between two layers of liquid each having area of A , separated by a distance dx and having velocity gradient, dv/dx is expressed as

$$f \propto A \frac{dv}{dx} \text{ or } f = \eta A \frac{dv}{dx}$$

Here η = coefficient of viscosity and its units are

$$\eta = \frac{f \cdot dx}{A \cdot dv} = \frac{\text{dyne} \times \text{cm}}{\text{cm}^2 \times \text{cms}^{-1}} = \text{dyne cm}^{-2} \text{s} = 1 \text{ poise}$$

In fundamental units,

$$1 \text{ poise} = 1 \text{ g cm}^{-1} \text{s}^{-1}$$

S.I. units of viscosity are Pa s or Nm^{-2} or $\text{kg m}^{-1} \text{s}^{-1}$. Commonly used unit poise is one tenth of the S.I. unit.

i. **Effect of temperature on viscosity:** Viscosity decreases with increase in temperature. The relationship between coefficient of viscosity, η and absolute temperature T is

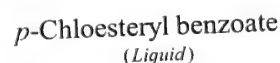
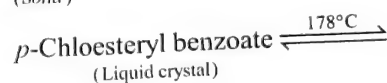
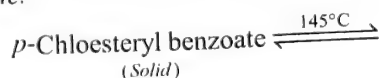
$$\eta = Ae^{E_a/RT}$$

where A and E_a are constants for a given liquid.

ii. **Effect of pressure on viscosity:** Viscosity increases with increase in pressure.

52. **Liquid crystals:** There are certain solids which when heated undergo two sharp phase transformations one after the other. Such solid first fuse sharply yielding turbid liquids and then further heating to a higher temperature these sharply change into clear liquids. The first temperature at which solid changes into turbid liquid is known as **transition point** and the second temperature at which turbid liquid changes into clear liquid is known as **melting point**. Some substance showing liquid crystal character are:

p-chloesteryl benzoate, *p*-Azoxyanisole, Diethylbenzidine etc.



A liquid crystal reflects only one colour, when white light falls on it. If the temperature is changed it reflects different colour light. So such liquid crystals can be used to detect even small temperature changes. The liquid crystals are of two types:

(i) **Nematic liquid crystals (needle like)** and (ii) **Smectic liquid crystals (soap like)**

53. **Surfactants:** These are surface active agents which decreases the surface tension of water e.g., soaps and detergents.

54. **Trouton's rule:** The molar heat of vapourisation of a liquid expressed in Joules divided by the normal boiling point of the liquid on the absolute scale is approximately equal to 88.

$$\frac{\Delta H}{T_b} \approx 88 \text{ JK}^{-1} \text{mol}^{-1} \text{ (21 cal K}^{-1} \text{mol}^{-1})$$

55. Liquid drops are spherical due to surface tension forces.

56. **Guidberg's rule:** According to this rule, the normal boiling point (T_b) of the liquid is nearly two-third of its critical temperature (T_c) when both are expressed on the absolute scale

$$T_b = \frac{2}{3} T_c$$

57. **Fluidity:** The reciprocal coefficient of viscosity is known as **fluidity** of the liquid.

$$\phi = \frac{1}{\eta}$$

- 58. Superfluidity:** Fluidity is a property by virtue of which liquids have a tendency to flow. Lesser the viscosity more is the fluidity. Certain liquids have almost no viscosity and therefore such liquids can act as super fluids i.e., there is effectively no effective resistance to their flow. Such liquid when kept in a container goes uphill (i.e., defies gravity) and flows out of the vessel. Such a superfluid state of matter is sometimes referred to as another state of matter. One such superfluid liquid is helium II—an allotropic form of helium. Helium I (He I) at 4.12 K is normal liquid, but on cooling to 2.178 K, another allotrope of helium (He II) appears. The transition from He I to He II is accompanied by a sharp transition in physical properties. For example, He II expands on cooling, has a thermal conductivity many hundreds of times greater than that of copper at room temperature and has no viscosity under certain conditions. Under such conditions, He II can act as a superfluid.

FORMULAE:

1. No. of moles of gas

$$n = \frac{\text{Mass in gms}}{\text{Mol. mass}} \text{ or } = \frac{\text{Volume in mL}}{22400}$$

$$\text{or } = \frac{\text{Number of molecule}}{6.02 \times 10^{23}}$$

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 = 10^3 \text{ L} = 10^3 \text{ dm}^3$$

$$1 \text{ atm} = 76 \text{ cm Hg} = 760 \text{ mm Hg} = 760 \text{ torr} \\ = 101325 \text{ Pa or Nm}^{-1} = 10^5 \text{ Pa} = 10^2 \text{ kPa}$$

$$0^\circ\text{C} = 273 \text{ K or } t^\circ\text{C} = (273 + t) \text{ K}$$

$$t^\circ\text{C} = \frac{5}{9} (^\circ\text{F} - 32)$$

2. Boyle's law equation:

$$V \propto \frac{1}{P} \text{ or } PV = \text{constant or } P_1 V_1 = P_2 V_2 \\ \text{(at constant } T \text{ and } n)$$

3. Charle's law equation:

$$V \propto T \text{ or } \frac{V}{T} = \text{constant or } V_1/T_1 = V_2/T_2 \\ \text{(at constant } P \text{ and } n)$$

4. Pressure law (Amonto' law equation):

$$P \propto T \text{ or } \frac{P}{T} = \text{constant or } \frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ (at constant } V \text{ and } n)$$

5. Avogadro's law:

$$V \propto n$$

6. Equation of state (ideal gas)

$$PV = nRT$$

7. Values of R :

$$0.0821 \text{ L-atm K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1} \\ = 8.314 \text{ JK}^{-1} \\ = 1.987 (\approx 2) \text{ cal K}^{-1} \text{ mol}^{-1}$$

8. General gas equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

9. Kinetic gas equation:

$$PV = \frac{1}{3} mNa^2$$

10. van der Waal equation of state:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

11. Graham's law of diffusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{Mw_2}{Mw_1}} = \sqrt{\frac{d_2}{d_1}}$$

12. Dalton's law of partial pressure:

$$P = p_1 + p_2 + p_3 + \dots$$

13. Partial pressure of any component (say A):

$$p_A = x_A \cdot P$$

where x_A is mole fraction of A and P is total pressure.

14. Molar mass and density:

$$d = \frac{PMw}{RT}$$

15. Average kinetic energy of gas:

$$\text{K.E.} = \frac{3}{2} kT$$

where $k = \frac{R}{N_A}$ is known as Boltzmann constant.

16. Root mean square velocity:

$$u_{\text{rms}} = \sqrt{3RT/Mw}$$

17. Most probable velocity:

$$\alpha = \sqrt{2RT/Mw}$$

18. Average velocity:

$$\bar{v} = \sqrt{8RT/\pi Mw}$$

19. Relationship between velocities:

$$u : \bar{v} : \alpha = \sqrt{3} : \sqrt{8/\pi} = 1.224 : 1.128 : 1$$

20. Compressibility factor:

$$Z = \frac{PV}{nRT}$$

21. Collision frequency:

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{v} N^2$$

22. Mean free path:

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n}$$

23. Critical temperature:

$$T_c = 8a/27 Rb$$

24. Critical pressure:

$$P_c = a/27b^2$$

25. Critical volume:

$$V_c = 3b$$

26. Relation between critical constants:

$$P_c V_c = \frac{3}{8} RT_c$$

27. Boyle's temperature

$$T_b = a/Rb$$

28. $C_p - C_v = R$... for 1 mole of gas

29. $C_p/C_v = \gamma = 1.66$ (for monoatomic gas)
 $= 1.40$ (for diatomic gas)
 $= 1.30$ (for triatomic gas)

30. Boltzmann constant (k) = $\frac{R}{N_A} = \frac{8.314 \text{ JK}^{-1}}{6.022 \times 10^{23} \text{ molecules}}$
 $= 1.38 \text{ JK}^{-1} \text{ molecule}^{-1}$

31. Loschmidt number = $2.768 \times 10^{19} \text{ cm}^{-3}$. (It is the number of molecules present in 1 cm^3 of a gas or vapour at STP).

5.1 INTRODUCTION

In previous chapters, we learnt about the properties of a single particle of matter such as atomic size, ionization enthalpy, electronic charge density, molecular shape and polarity. Most of the observable characteristics of chemical systems with which we are familiar represent bulk properties of matter, i.e., the properties associated with a collection of a large number of atoms, ions, or molecules. For example, an individual molecule of a liquid does not boil but the bulk boils. A collection of water molecules can make a surface wet but individual molecules cannot. Water can exist as ice, which is a solid. It can exist as liquid, or it can exist in the gaseous state as water vapour or steam. Physical properties of ice, water, and steam are very different. In all the three states, chemical composition of water remains the same, i.e., H_2O . Characteristics of the three states of water depend on the energies of molecules and the manner in which water molecules aggregate. Same is true for other substances also.

Chemical properties of a substance do not change with change in its physical state, but the rate of chemical reactions depends upon the physical state. Many times in calculations dealing with data of experiments we require knowledge of the states of matter. Therefore, it becomes necessary for a chemist to know the physical state of matter.

Matter can be classified into three categories depending upon its physical states, namely, solid, liquid, and gaseous states.

- Solid state:** The matter in solid state possesses a definite volume, shape, and mass. Some common examples are table, chair, common salt, silver, etc.
- Liquid state:** The matter in liquid state possesses a definite volume and mass but no definite shape. In fact, it acquires the shape of the container. Some examples are milk, water, alcohol, etc.
- Gaseous state:** The matter in gaseous state has neither definite volume nor a definite shape, but it has a definite mass. It acquires the shape and volume of the container. Some common examples are air, oxygen, hydrogen, sulphur dioxide, etc.

Recent research has led to the discovery of fourth and fifth states of matter.

The *fourth state* called the *plasma state* refers to the super heated gaseous state consisting of a mixture of electrons and positively charged ions with unusual properties. It is found at extremely high temperatures such as in the interior of sun or stars or in intense electrical fields such as in a discharge tube. Astronomers claim that 99% of all matter in the universe is present in the plasma state.

The *fifth state* refers to the super cooled solid state in which atoms lose their separate identity, get condensed, and behave like a single super atom. The study of this phenomenon is based upon the Bose-Einstein condensation (BEC) concept developed in 1924.

5.2 THREE STATES OF MATTER AND CONDITIONS OF TEMPERATURE AND PRESSURE

Almost all substances exist in three states under appropriate conditions of temperature and pressure. The physical state of a substance is largely determined by temperature and pressure considerations. For example, a substance is said to be

- Solid if its melting point is above the room temperature at the atmospheric pressure.
- Liquid if its melting point is below the room temperature and its boiling point is above the room temperature.
- Gas if its boiling point is below the room temperature at the atmospheric pressure.

It has been found that in most cases, a given substance can be made to exist in any one of the three states under different conditions of temperature and pressure. For example, water is a liquid under ordinary conditions of temperature and pressure, but it can be converted into steam (gas) at 100°C under one atmospheric pressure or into ice (solid) by cooling to 0°C under one atmospheric pressure.

A given substance can also simultaneously exist in all the three states under certain specified conditions of temperature and pressure. For example, water exists simultaneously in all the three phases, viz. ice (solid), water (liquid), and water vapour (gas), at its freezing point, i.e., 0°C , and 4.58 mm Hg pressure. This equilibrium condition of water is referred to as triple point.

The important differences among the three states of matter, namely, solid, liquid, and gas, are given in Table 5.1.

Table 5.1 Comparison of the characteristics of a solid, liquid, and gas

	Solids	Liquids	Gases
1.	Molecules are closely packed.	Molecules are less closely packed.	Molecules are sufficiently apart from one another.
2.	Mutual forces of attraction are the strongest.	Mutual forces of attraction are weaker than those in solids.	Mutual forces of attraction are almost negligible.
3.	The density of solids is high.	The density of liquids is lower than that of solids but much higher than that of gases.	Gases generally have low densities.

Table 5.1 continued...

	Solids	Liquids	Gases
4.	The positions of molecules in the crystal lattice are fixed, and hence solids do not have translatory or rotatory motion but only possess vibratory motion.	Molecules of liquids have greater freedom of movement. They have some translatory and rotatory motions in addition to vibratory motion.	Molecules of gases have large rotatory, vibratory, and translatory motions.
5.	Molecules of solids possess least energy.	Molecules of liquids have higher energies than those of solids.	Gas molecules are most energetic.
6.	Solids have both definite shape and definite volume.	Liquids do not have definite shape but have definite volume.	Gases have neither definite shape nor definite volume.
7.	Solids possess least compressibility and thermal expansion.	Liquids have slightly higher compressibility and thermal expansion than those of solids.	Gases possess high compressibility and thermal expansion.

The physical state of existence of a substance at a given condition is a balance between the thermal energy and intermolecular interactions. It is because both these factors affect molecular motion, which further determines the physical state. Let us now learn about the nature and types of intermolecular forces.

5.3 INTERMOLECULAR FORCES

Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between two oppositely charged ions and the forces that hold atoms of a molecule together, i.e., covalent bonds.

Attractive intermolecular forces are known as *van der Waals forces*, in honour of Dutch scientist Johannes van der Waals (1837–1923), who explained the deviation of real gases from the ideal behaviour through these forces. We will learn about this later in this chapter. van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole–dipole forces, and dipole–induced dipole forces. A particularly strong type of dipole–dipole interaction is hydrogen bonding. *Only a few elements can participate in hydrogen bond formation; therefore, it is treated as a separate category.*

At this point, it is important to note that attractive forces between an ion and a dipole are known as ion–dipole forces and ion induced dipoles, these are not van der Waals forces.

5.3.1 DISPERSION FORCES OR LONDON FORCES

Dispersion forces are interparticle forces among the monatomic or non-polar molecules such as N_2 , He, CO_2 , etc.

Atoms and non-polar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood from the following illustration. Suppose we have two atoms A and B in the close vicinity of each other [Fig. 5.1 (a)]. It may so happen that electronic charge distribution in one of the atoms, say A, becomes momentarily unsymmetrical, i.e., the charge cloud is more on one side than the other [Fig. 5.1(b, c)]. This results in the development of instantaneous dipole on the atom A for a very short time. This instantaneous or

transient dipole distorts the electron density of the other atom B, which is close to it, and as a consequence a dipole is induced in the atom B.

The temporary dipoles of atoms A and B attract each other. Similarly, *temporary dipoles are induced in molecules also*. This force of attraction was first proposed by the German physicist Fritz London, and for this reason the force of attraction between two temporary dipoles is known as *London force*.

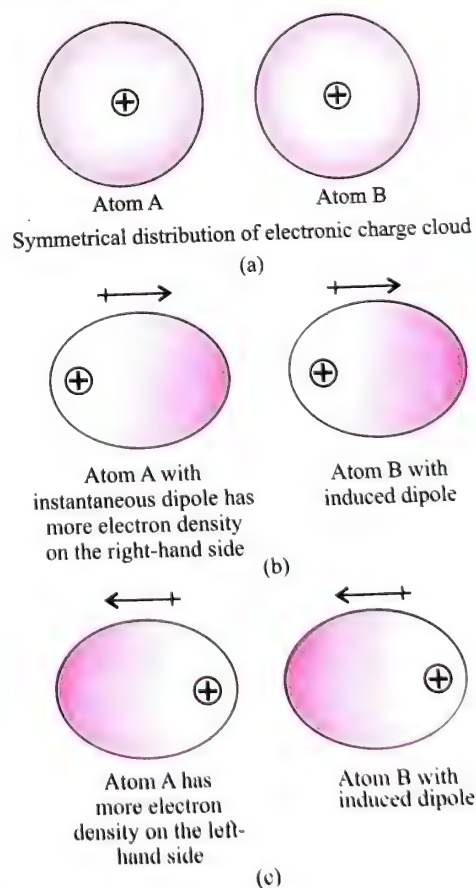


Fig. 5.1 Dispersion forces or London forces between two atoms

Another name of this force is *dispersion force*. These forces are always attractive. In these forces, the interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$, where r is the distance between two particles). These forces are important only at short distances

(~ 500 pm), and their magnitude depends on the polarisability of the particle.

The strength of these forces depends upon the following factors:

- Molecular size (molar mass)—Molecules having larger size or molar mass have higher magnitude of London forces.
- Number of electrons—Molecules with higher number of electrons have higher magnitude of London forces compared to molecules with lesser number of electrons.
- Surface area of molecule—With an increase in surface area, the strength of London forces also increases.

For example, boiling point increases from CH_4 to GeH_4 , i.e., CH_4 (112 K) < SiH_4 (161 K) < GeH_4 (183 K).

- Molecular mass and number of electron increase
- Intermolecular forces increase
- Boiling points increase

5.3.2 DIPOLE-DIPOLE FORCES

Dipole-dipole forces act among molecules possessing permanent dipole. Ends of dipoles possess 'partial charges' and these charges are shown by Greek letter delta (δ). Partial charges are always less than the unit electronic charge (1.6×10^{-19} C). Polar molecules interact with neighbouring molecules. Fig. 5.2(a) shows electron cloud distribution in the dipole of hydrogen chloride, and Fig. 5.2(b) shows dipole-dipole interaction between two HCl molecules. This interaction is stronger than the London forces but is weaker than the ion-ion interaction because only partial charges are involved. The attractive forces decrease with an increase in distance between the dipoles. As in the above case, the interaction energy is inversely proportional to the distance between two polar molecules. Dipole-dipole interaction energy between two stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between two rotating polar molecules is

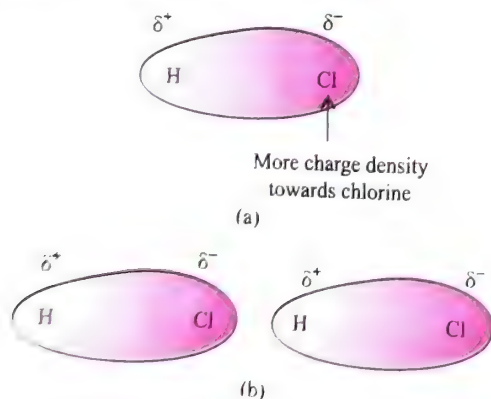


Fig. 5.2. (a) Distribution of electron cloud in HCl, a polar molecule
(b) Dipole-dipole interaction between two HCl molecules

proportional to $1/r^6$, where r is the distance between the two molecules. Besides dipole-dipole interaction, polar molecules can also interact by London forces. The cumulative effect is that total intermolecular forces in polar molecules increase.

5.3.3 DIPOLE-INDUCED DIPOLE FORCES

This type of attractive forces operate between polar molecules having permanent dipole ($\mu > 0$) and molecules lacking permanent dipole ($\mu = 0$). Permanent dipole of a polar molecule induces a dipole on the electrically neutral molecule by deforming its

electronic cloud (Fig. 5.3). Thus an induced dipole is developed in the other molecule. In this case also, interaction energy is proportional to $1/r^6$, where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.

As the size of molecule/atom increases, it can be easily polarised.

High polarisability increases the strength of attractive interactions.

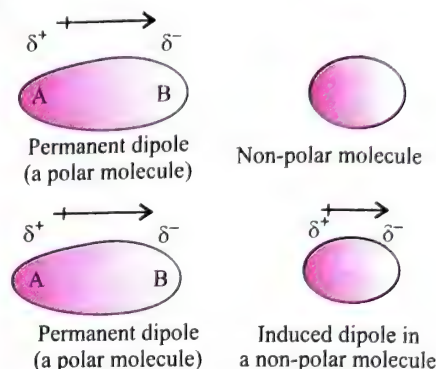


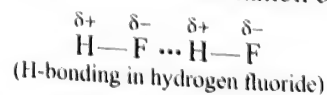
Fig. 5.3 Dipole-induced dipole interaction between permanent dipole and induced dipole

In this case also, the cumulative effect of dispersion forces and dipole-induced dipole interactions exists. The existence of these forces was studied by Debye (1920), and this effect was termed induction effect.

5.3.4 HYDROGEN BONDS

This is a special type of dipole-dipole interaction operating between molecules in which hydrogen atom is covalently bonded to a highly electronegative atom such as nitrogen (N), oxygen (O), or fluorine (F). Although hydrogen bonding is regarded as being limited to N, O, and F, but species such as Cl^- may also participate in hydrogen bonding. In the highly polar $\text{N}-\text{H}$, $\text{O}-\text{H}$ or $\text{H}-\text{F}$ bond, the bond pair of electrons forming covalent bond is displaced towards the electronegative atom, i.e., N, O, or F. When the solitary electron of H atom lies away, it behaves almost as a paired proton and exerts a strong electrostatic force of attraction on the electronegative atom of the other molecule in vicinity.

The energy of hydrogen bond varies between 10 and 100 kJ mol^{-1} . This is a significant amount of energy; therefore, hydrogen bonds are powerful forces in determining the structure and properties of many compounds such as proteins and nucleic acids. The strength of hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of the other molecule. The following diagram shows the formation of hydrogen bond.



Repulsive interaction between molecules/atoms: Intermolecular forces discussed so far are all attractive. Molecules also exert repulsive forces on one another. When two molecules are brought into contact, repulsion between their electron clouds as well as between their nuclei comes into play. The magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason why liquids and solids are hard to compress. In these states, molecules are already in close

contact; therefore, they resist further compression as that would result in an increase in repulsive interactions.

5.4 THERMAL ENERGY

Thermal energy is the energy of a body arising from the motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of the average kinetic energy of the particles of matter and is thus responsible for the movement of particles. This movement of particles is called thermal motion.

5.4.1 INTERMOLECULAR FORCES AND THERMAL ENERGY

We have already learnt that intermolecular forces tend to keep molecules together but thermal energy tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

In the gaseous state, molecular interactions are very weak. Gas molecules do not cling together as in liquids or solids unless the thermal energy of the gas is reduced by lowering its temperature. A decrease in thermal energy causes molecules to come close, and they gradually develop intermolecular attraction till the gas condenses first into liquid and finally into solid. Gases do not liquefy only on compression, although molecules come very close to each other and intermolecular forces operate to the maximum. However, by reducing the thermal energy of molecules by lowering the temperature, gases can be very easily liquefied.

In the liquid state, a fine balance exists between attractive forces and thermal energy. As a result, molecules can break away from one another and at the same time get attracted to other molecules. An increase in temperature results in an increase in thermal energy, and ultimately a stage reaches when the molecules fall apart and behave almost as independent entities. This stage is referred to as gaseous state. On the other hand, a decrease in temperature decreases thermal energy. On further compression, the intermolecular interaction increases. At this stage, the molecules of liquid cling closely and this stage is referred to as solid state.

In the solid state, molecular interactions are very strong, but the molecular motion is restricted to oscillatory or vibratory movement about their mean position. The molecules possess low thermal energy and, therefore, cannot break molecules free from mutual attraction. When we heat a solid, thermal energy gradually increases, which weakens the intermolecular forces and causes them to move apart. When the average distance between the molecules increases beyond 10^{-7} cm, the solid melts into liquid. Further rise in temperature results in further increase in thermal energy, which further weakens the intermolecular forces and causes them to move apart and results in gaseous state.

Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows:

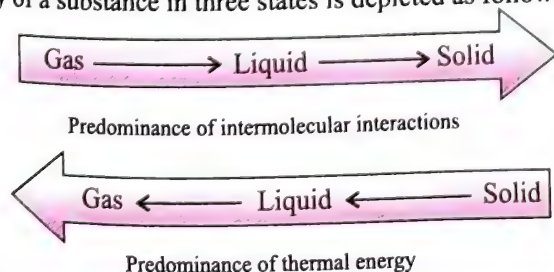


Fig. 5.4 Predominance of intermolecular interactions and thermal energy

5.5 GASEOUS STATE

In all the three states of matter, the gaseous state is the simplest state of matter. Throughout our life we remain immersed in the ocean of air which is a mixture of gases. The thick blanket of air surrounding the earth is called atmosphere. We spend our life in the lowermost layer of the atmosphere called troposphere. The atmosphere is very vital for our life as it shields us from harmful radiations and contains substances such as dioxygen, dinitrogen, carbon dioxide, water vapour, etc.

Molecules of various gases present in the atmosphere are under the constant pull of the gravitational force of the earth. As a result, the atmosphere is dense near the surface of the earth than on high altitudes.

The gaseous state is characterised by the following physical properties:

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than solids and liquids.
- Gases do not have fixed volume and shape. They acquire the shape and volume of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

It is interesting to note that of the all known elements only 11 elements exist in gaseous state under normal condition of temperature (25°C) and pressure (1 bar). These are given in Fig. 5.5.

Group number	1		15	16	17	18
	H					He
			N	O	F	Ne
					Cl	Ar
						Kr
						Xe
						Rn

Fig. 5.5 Eleven elements that exist as gases

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour is governed by same general laws discovered as a result of experimental studies. These laws are relationships between measurable properties of gases. Some of these properties such as pressure, volume, temperature, and mass are very important because relationships between these variables describe the state of the gas. Interdependence of these variables leads to the formulation of gas laws.

Before we take up the detailed study of gas laws, let us look into some of these measurable properties of gases such as mass, volume, pressure, and temperature.

5.5.1 MEASURABLE PROPERTIES OF GASES

The state of a gas is described by the relationship of variables such as mass, volume, temperature, and pressure. These are important measurable properties.

- a. **Mass:** The mass of a gas can be experimentally determined by weighing the container containing the gas and then taking the weight of the empty container. The difference in the two weights gives the mass of the gas. The amount of the gas can be expressed in terms of its number of moles by using the following relationship:

$$\text{Number of moles} = \frac{\text{Mass in gram}}{\text{Molar mass}}$$

- b. **Volume:** As a gas fills the whole of the vessel in which it is put, the volume of the gas is equal to the volume of the container, which can be calculated from the dimensions of the container.

The SI unit of volume is m^3 , but this is a big unit. Hence, the units commonly used are cm^3 or dm^3 . The units millilitre and litre are also continued to be used, generally in expressing volumes of liquids and solutions. These units are inter-related as follows:

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3$$

$$1 \text{ mL} = 1 \text{ cm}^3$$

$$1 \text{ L} = 10^3 \text{ cm}^3 = 1 \text{ dm}^3$$

- c. **Pressure:** Gases exert outward force on the walls of the container in which they are enclosed. The outward force experienced by the walls is due to the bombardment of gas molecules on them. This outward force per unit area of the walls is termed as *gas pressure*.

Units of gas pressure: Pressure is force per unit area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

By definition,

$$\text{Force} = \text{Mass} \times \text{Acceleration}$$

$$= \frac{\text{Mass} \times \text{Velocity}}{\text{Time}} = \frac{\text{Mass} \times \text{Distance}}{\text{Time} \times \text{Time}} = \frac{\text{kg} \times \text{m}}{\text{s} \times \text{s}}$$

Thus, the SI unit of force is kg m s^{-2} which is called newton (N).

$$1 \text{ N} = 1 \text{ kg m s}^{-2}$$

Putting SI units of force (N) and area (m^2), we get the SI unit of pressure as N/m^2 or N m^{-2} . This SI unit of pressure is called pascal (Pa) in the honour of French mathematician and physicist Blaise Pascal.

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

Now, $1000 \text{ Pa} = 1$ kilo pascal, abbreviated as kPa.

For gases, this unit of pressure is very small. Hence, pressure is generally expressed in terms of a bigger unit called *bar*. One bar represents 100 kilo pascal. Thus

$$1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$$

It may be noted that the older unit of pressure was atmosphere which is abbreviated as *atm*. The relationship between these units is as follows:

$$1 \text{ atm} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa}$$

$$\text{or } 1 \text{ bar} = 0.987 \text{ atm}$$

Atmospheric pressure: The force experienced by any area of the earth exposed to the atmosphere is equal to the weight of column of air above it. This force per unit area of the earth is called atmospheric pressure. The value of atmospheric pressure varies with the location of the place, temperature, and weather conditions. It may be noted that we do not feel the pressure exerted by the atmosphere because we are physiologically well adapted to it just like a fish keeps moving freely under the pressure of water.

Measurement of atmospheric pressure: The atmospheric pressure can be measured by a simple device called barometer. A simple barometer can be made by filling mercury in a tube (longer than 76 cm) closed at one end and inverting it in an open vessel containing mercury. The mercury level in the tube adjusts itself and stands approximately 76 cm above the level of mercury in the open vessel.

The weight of the mercury column held in the tube gives a measure of the atmospheric pressure. The height of the column decreases when the pressure of the atmosphere decreases, whereas the height of the column increases with on increase in the atmospheric pressure.

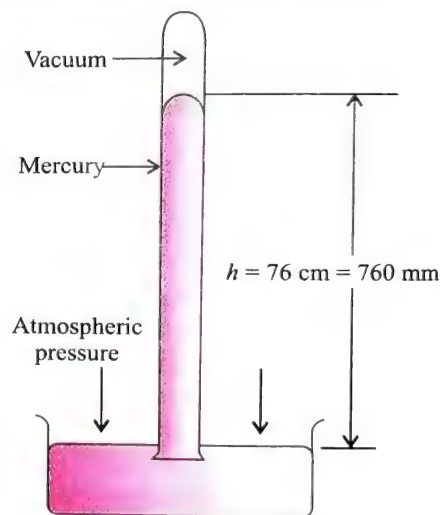


Fig. 5.6 A mercury barometer

The atmospheric pressure P can be mathematically calculated as follows:

$$P = \frac{\text{Downward force of Hg column}}{\text{Area of cross section of Hg column}}$$

$$= \frac{\text{Mass of Hg column} \times \text{Acceleration due to gravity}}{\text{Area of cross section of Hg column}} = \frac{mg}{a}$$

$$\begin{aligned} \text{Now, mass of Hg column (m)} &= \text{Volume} \times \text{Density} \\ &= \text{Area} \times \text{Height} \times \text{Density} \\ &= a \times h \times d \end{aligned}$$

Thus, pressure,

$$P = \frac{a \times h \times d \times g}{a} = hdg$$

As the density of mercury (ρ) and the acceleration due to gravity (g) remain constant, measurement of the length of the Hg column gives the value of the atmospheric pressure. According to an international agreement, a *standard atmospheric pressure* (1 atm) is the pressure exerted by exactly 76 cm of mercury column at 0°C (273.15 K) measured at sea level where standard gravity is 9.806 m s^{-2} , with the density of mercury being 13.596 g cm^{-3} . It is exactly equal to 760 mm Hg. The unit mm Hg is also called *torr*, after the name of Italian scientist Evangelista Torricelli who invented barometer. In short,

$$1\text{ atm} = 76.0\text{ cm of mercury}$$

$$= 760\text{ mm of mercury} = 760\text{ torr}$$

The numerical value of 1 pressure can be calculated as follows:

$$P = h\rho g$$

$$= (0.76\text{ m})(13.596 \times 10^3\text{ kg m}^{-3})(9.806\text{ m s}^{-2})$$

$$= 101325\text{ kg m}^{-1}\text{ s}^{-2}\text{ or }101325\text{ N m}^{-2}$$

$$= 101325\text{ pascal (Pa)}$$

$$= 101.325\text{ kilopascal (kPa)}$$

In brief:

$$0.987\text{ atm} = 1\text{ bar} = 10^5\text{ Pa} = 100\text{ kPa} = 14.509\text{ psi}$$

Measurement of gas pressure: Pressures other than atmospheric pressure are measured by device called *manometer*. There are two types of manometer: *open-end* and *closed-end* manometers.

i. **Open-end manometer:** It consists of a U-tube partially filled with mercury. One limb of the tube is shorter than the other limb. The shorter limb is connected to a vessel containing gas, whereas the longer limb is open as shown in Fig. 5.7. The mercury in the longer tube is subjected to the atmospheric pressure, while the mercury in the shorter tube is subjected to the pressure of the gas.

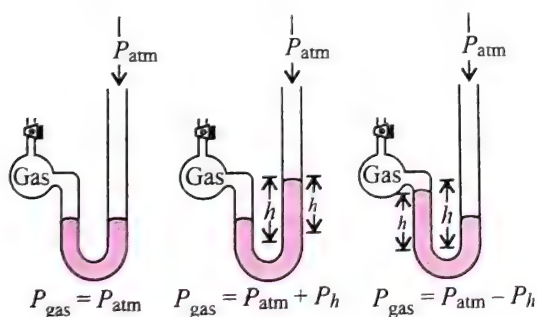


Fig. 5.7 Measurement of gas pressure

There are three possibilities described as follows:

1. If the level of Hg in the two limbs is same,
gas pressure (P_{gas}) = atmospheric pressure (P_{atm})
2. If the level of Hg in the longer limb is higher,
gas pressure (P_{gas}) = P_{atm} + (difference between the two levels)
$$= P_{\text{atm}} + P_h$$
3. If the level of Hg in the shorter limb is higher,
gas pressure (P_{gas}) = P_{atm} - (difference between the two levels)
$$= P_{\text{atm}} - P_h$$

ii. **Closed-end manometer:** It is generally used to measure low gas pressures. It also consists of a U-tube with one limb shorter than the other and partially filled with mercury, as shown in Fig. 5.8. The space above the mercury at the closed end is completely evacuated. The shorter limb is connected to a vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.

$$\text{Gas pressure } (P_{\text{gas}}) = (\text{difference in the Hg level in the two limbs})$$

$$\text{or } P_{\text{gas}} = P_h$$

It may be noted that an open-end manometer is better for measuring pressures equal to or greater than the atmospheric pressure. On the other hand, closed-end manometer is suited to measure pressures below the atmospheric pressure.

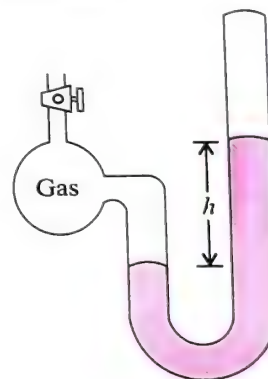


Fig. 5.8 Closed-end manometer

d. **Temperature:** In general, temperature may be defined as the *degree of hotness*. Temperature can be measured in terms of the effect that its change produces on other measurable properties such as expansion of objects. Expansion of mercury is commonly used for the measurement of temperature. One of the common temperature measuring devices is a thermometer. It has a mercury column in a thin capillary tube. The length of the mercury column changes with a change in temperature.

Various Temperature Scales

- **Celsius scale of temperature ($^\circ\text{C}$):** This is the most common scale of temperature, which was earlier known as the centigrade scale. In this scale, at one atmospheric pressure the melting point of ice is 0°C , whereas the boiling point of water is 100°C . The range between these two points has been divided into hundred equal parts. Each division corresponds to one degree in the Celsius scale. As the zero in the Celsius scale is arbitrarily fixed, it is possible to have temperature below the freezing point. It may appear that the Celsius scale can be extended to negative temperature indefinitely, but experimental behaviour of gases shows that a temperature below -273.15°C is impossible to be attained.
- **Kelvin scale of temperature (K):** This scale of temperature is quite significant and is very useful for scientific work, which can be justified by

thermodynamic arguments. It is, therefore, also called the thermodynamic scale of temperature. Kelvin is also the SI unit of temperature. The zero point on the Kelvin scale is equal to the lowest possible temperature (-273.15°C) and is known as the absolute zero (0 K). A temperature in Celsius scale can be converted into that in Kelvin scale by adding 273.15 (or 273 for the sake of simplicity) to it.

$$\text{K} = ^{\circ}\text{C} + 273.15$$

- **Fahrenheit scale ($^{\circ}\text{F}$):** This scale is based on taking the freezing point of water at 1 atm pressure as 32°F and the boiling point of water at 212°F . The entire range is divided into 180 equal parts.

Thus, 100 Celsius degrees = 180 Fahrenheit degrees

The relationship between Celsius and Fahrenheit scales is

$$^{\circ}\text{C} = \frac{5}{9}(^{\circ}\text{F} - 32) \text{ and } ^{\circ}\text{F} = \frac{9}{5}(^{\circ}\text{C}) + 32$$

A comparison between the three scales is given in Fig. 5.9.

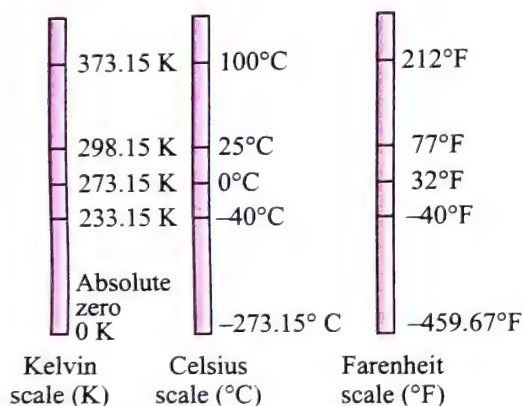


Fig. 5.9 Comparison of Kelvin, Celsius, and Fahrenheit scales of temperature

5.6 GAS LAWS

The gas laws are the result of extensive research on the physical properties of gases carried out by various scientists for several centuries.

5.6.1 BOYLE'S LAW (PRESSURE–VOLUME RELATIONSHIP)

The first quantitative relationship between the volume and pressure of a gas was studied experimentally by Robert Boyle in 1662. This law describes the pressure–volume relationship of gases at constant temperature. The law states that the volume of a fixed mass of gas is inversely proportional to its pressure at constant temperature.

The law can be demonstrated by a simple experiment as described below. A U-shape tube is filled partially with mercury as shown in Fig. 5.10. The pressure inside is increased by putting more mercury into the open limb. The volume of air enclosed in the space above the mercury in the shorter limb is noted each time. It is found that as pressure increases, the volume of enclosed air gradually decreases.

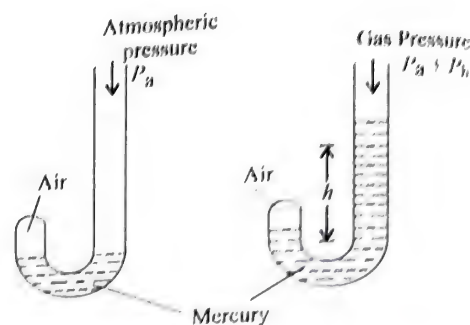


Fig. 5.10 Demonstration of Boyle's Law

MATHEMATICAL INTERPRETATION OF THE LAW

Mathematically, the law may be expressed as

$$P \propto \frac{1}{V} \text{ (at constant temperature and mass)} \quad \dots(i)$$

$$\text{or } P = K \times \frac{1}{V} \quad \dots(ii)$$

where K is the proportionality constant. The value of K depends upon the amount of gas, temperature of the gas, and the units in which P and V are expressed. On rearranging Eq. (ii), we get

$$PV = K \quad \dots(iii)$$

It means that at a constant temperature, the product of the pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes expansion so that the volume becomes V_2 and the pressure becomes P_2 , then according to Boyle's law

$$P_1 V_1 = P_2 V_2 = \text{constant} \quad (T \text{ and } n \text{ are constants})$$

$$\text{or } \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

The law can be experimentally verified by measuring the volumes of a given mass of gas at different pressures keeping the temperature constant. In each case, the product PV is found to be constant.

The values of pressures and volumes of a fixed mass (0.19 mol) of CO_2 at constant temperature 300 K are given in Table 5.2

Table 5.2 Effect of pressure on the volume of 0.09 mol of CO_2 gas at 300 K

Pressure (10^4 Pa)	Volume (10^{-3} m^3)	$1/V \text{ (m}^{-3}\text{)}$	$pV(10^2 \text{ Pa m}^3)$
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

GRAPHICAL REPRESENTATION OF BOYLE'S LAW

The law can also be illustrated by means of pressure–volume curves as shown in Fig. 5.11

- a. Fig. 5.11(a) shows the plot of V vs P at a particular temperature. It shows that as P increases, V decreases.

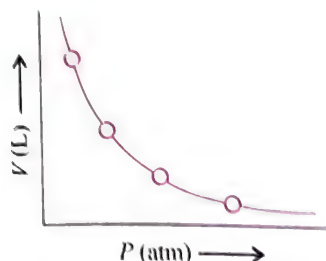


Fig. 5.11(a) Plot of V against P

- b. Fig. 5.11(b) shows the plot of PV vs P at a particular temperature. It indicates that PV values remain constant in spite of a regular increase in P . The curve obtained by plotting PV against P at a particular temperature is called *isotherm*. The higher curve corresponds to higher temperature.

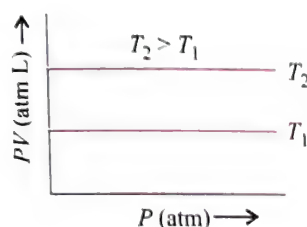


Fig. 5.11(b) Plot of PV against P

- c. Fig. 5.11(c) gives the variation of P against $1/V$. The straight line indicates that $1/V$ regularly increases with an increase in P .

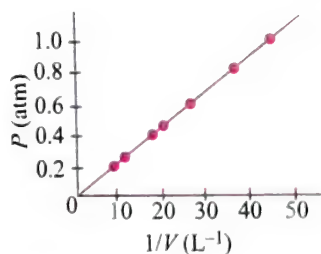


Fig. 5.11(c) Plot of P against $1/V$

- d. Fig. 5.11(d) gives P - V isotherm at different temperature.

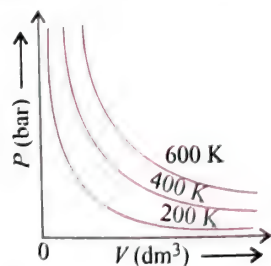


Fig. 5.11(d) Graph of P vs V of a gas at different temperatures

Following are some other curves for Boyle's law.

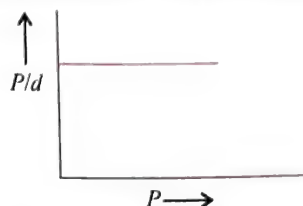


Fig. 5.12(a) Graph of P/d vs P

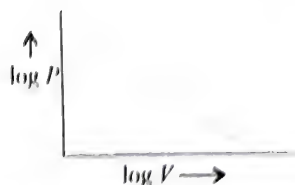


Fig. 5.12(b) Graph of $\log P$ vs $\log V$

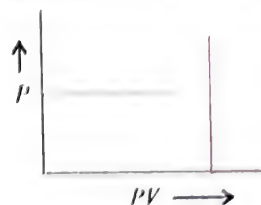


Fig. 5.12(c) Graph of P vs PV

PRACTICAL IMPORTANCE OF BOYLE'S LAW

The Boyle's law expresses in quantities an important experimental fact that gases are compressible. When a given mass of gas is compressed, the same number of molecules occupy a smaller space. This means that the gas becomes denser at a higher pressure. For example, air at the sea level is denser because it is compressed by the mass of air above it. However, density and pressure decrease with an increase in altitude. The atmospheric pressure at Mount Everest is only about 0.5 atm. The decrease in pressure at high altitudes causes altitude sickness (sluggish feeling, headache, etc.) due to a decrease in the oxygen intake in each breath.

The inside of jet airplanes, which normally fly at a height of about 10000 m, is specially maintained at normal pressure. The planes are also equipped with emergency oxygen supply in case the pressure falls.

A relationship can be obtained between the density and pressure of a gas by using Boyle's law as follows:

By definition, density d is related to mass m and volume V by the relation $d = m/V$. If we put the value of V from Boyle's law equation in this equation, we obtain the following relationship:

$$d = \left(\frac{m}{K} \right) P = K'P$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

ILLUSTRATION 5.1

A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure, the gas occupies 2.27 L volume, up to what volume can the balloon be expanded?

Sol. According to Boyle's law, $P_1V_1 = P_2V_2$

If P_1 is 1 bar, V_1 will be 2.27 L.

If $P_2 = 0.2$ bar, then

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1 \text{ bar} \times 2.27 \text{ L}}{0.2 \text{ bar}} = 11.35 \text{ L}$$

Since the balloon bursts at 0.2 bar pressure, the volume of the balloon should be less than 11.35 L.

ILLUSTRATION 5.2

A manometer is connected to a gas containing bulb. The open arm reads 40.0 cm where as the arm connected to the bulb reads 15.0 cm. If barometric pressure is 74.0 cm Hg, then what is the pressure of gas in bar?

Sol. Difference in mercury levels of two arms = 40.0 – 15.0 = 25.0 cm

Since level of Hg in the limb connected to gas bulb is lower than that in open limb, this means that gas pressure is more than the atmospheric pressure.

$$\therefore \text{Gas pressure} = \left(\begin{array}{c} \text{Barometric} \\ \text{pressure} \end{array} \right) + \left(\begin{array}{c} \text{Difference in} \\ \text{Hg levels} \end{array} \right)$$

$$= 74.0 \text{ cm} + 25.0 \text{ cm} = 99.0 \text{ cm}$$

$$\text{or } \frac{99.0}{76} \text{ atm or } \frac{99.0 \times 1.01325}{76} \text{ bar}$$

$$= 1.319 \text{ bar}$$

ILLUSTRATION 5.3

At fixed temperature and 600 mm pressure, the density of a gas is 42. At the same temperature and 700 mm pressure, what is the density of the gas?

Sol. According to Boyle's law,

$$P \propto \frac{1}{V} \quad (\text{at constant temperature})$$

$$\text{Density } (D) = \frac{\text{Mass } (m)}{\text{Volume } (V)}$$

$$\text{or } D \propto \frac{1}{V}$$

$$\therefore P \propto D$$

$$\text{or } \frac{P_1}{D_1} = \frac{P_2}{D_2}$$

$$\therefore D_2 = \frac{P_2 \times D_1}{P_1}$$

$$\text{Given } P_1 = 600, D_1 = 42, P_2 = 700$$

$$\therefore D_2 = \frac{700 \times 42}{600} = 49$$

Hence, the density of the gas is 49.

ILLUSTRATION 5.4

5 g of He at 27°C is subjected to a pressure change from 0.5 atm to 2 atm. The initial volume of the gas is 10 dm³. Calculate the change in volume of the gas.

Sol. Given that $P_1 = 0.5 \text{ atm}$, $P_2 = 2 \text{ atm}$, $V_1 = 10 \text{ dm}^3$, $V_2 = ?$

Using Boyle's relationship $P_1 V_1 = P_2 V_2$, we get

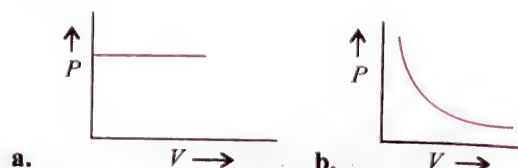
$$V_2 = \frac{P_1 V_1}{P_2} = \frac{0.5 \times 10}{2} = 2.5 \text{ dm}^3$$

Hence change in volume

$$\Delta V = V_1 - V_2 = 10 - 2.5 = 7.5 \text{ dm}^3$$

ILLUSTRATION 5.5

Among the plots of P vs V given below, which one corresponds to Boyle's law?

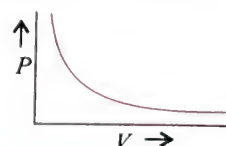


Sol. According to Boyle's law,

$$V \propto \frac{1}{P}$$

$$\text{or } PV = K \text{ (constant)}$$

Hence, the plot of P vs V will be



So, the answer is (b).

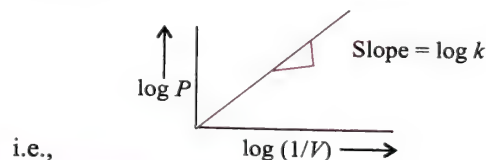
ILLUSTRATION 5.6

Draw a graph of $\log P$ and $\log (1/V)$ for a fixed amount of gas at constant temperature.

Sol. According to Boyle's law, $P = k/V$. Taking log of both sides, we get

$$\log P = \log (1/V) + \log k$$

Comparing it to $y = mx + c$, we find that the graph of $\log P$ vs $\log 1/V$ should be a straight line with slope equal to k , i.e.,



i.e.,

ILLUSTRATION 5.7

What is the volume of a sample of oxygen at a pressure of 3.5 bar if its volume at 1 bar is 3.15 L at the same temperature?

Sol. Here, $P_1 = 1 \text{ bar}$, $P_2 = 3.5 \text{ bar}$, $V_1 = 3.15 \text{ L}$, $V_2 = ?$

From Boyle's law equation $P_1 V_1 = P_2 V_2$, we get

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{1.00 \text{ bar} \times 3.15 \text{ L}}{3.5 \text{ bar}} = 0.90 \text{ L}$$

ILLUSTRATION 5.8

A gas occupies a volume of 2.5 L at $9 \times 10^5 \text{ N m}^{-2}$. Calculate the additional pressure required to decrease the volume of the gas to 1.5 L, keeping temperature constant.

Sol. Here, $P_1 = 9 \times 10^5 \text{ N m}^{-2}$, $P_2 = ?$

$$V_1 = 2.5 \text{ L}, V_2 = 1.5 \text{ L}$$

From Boyle's law equation $P_1 V_1 = P_2 V_2$, we get

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{9.0 \times 10^5 \text{ N m}^{-2} \times 2.5 \text{ L}}{1.5 \text{ L}} = 15 \times 10^5 \text{ N m}^{-2}$$

The additional pressure required is

$$15 \times 10^5 \text{ N m}^{-2} - 9 \times 10^5 \text{ N m}^{-2} = 6 \times 10^5 \text{ N m}^{-2}$$

ILLUSTRATION 5.9

A vessel of 120 mL capacity contains a certain mass of gas at 20°C and 750 mm pressure. The gas was transferred to a vessel whose volume is 180 mL. Calculate the pressure of the gas at 20°C .

Sol. Since a gas completely fills the vessel in which it is kept, we have

$$V_1 = 120 \text{ mL}, V_2 = 180 \text{ mL}$$

$$P_1 = 750 \text{ mm}, P_2 = ? \text{ mm}$$

Since the temperature remains constant, by applying Boyle's law, we get

$$P_1 V_1 = P_2 V_2$$

Substituting the corresponding values, we have

$$750 \times 120 = P_2 \times 180$$

$$\text{or } P_2 = \frac{750 \times 120}{180} = 500 \text{ mm}$$

Therefore, the pressure of the gas is 500 mm.

ILLUSTRATION 5.10

103 mL of carbon dioxide was collected at 27°C and 763 mm pressure. What will be its volume if the pressure is changed to 721 mm at the same temperature?

Sol. Given conditions Final conditions

$$V_1 = 103 \text{ mL}$$

$$V_2 = ? \text{ mL}$$

$$P_1 = 750 \text{ mm}$$

$$P_2 = 721 \text{ mm}$$

By applying Boyle's law since temperature is constant,

$$P_2 \times V_2 = P_1 \times V_1$$

Substituting the corresponding values, we have

$$721 \times V_2 = 763 \times 103$$

$$\text{or } V_2 = \frac{763 \times 103}{721} = 109 \text{ mL}$$

Therefore, the volume of carbon dioxide is 109 mL.

5.6.2 CHARLES' LAW (TEMPERATURE–VOLUME RELATIONSHIP)

This law describes the relationship between the volume and temperature of a gas at constant pressure. It was put forward by

French chemist Jacques Charles in 1767 and was further developed in 1802 by Joseph Gay-Lussac. This law can be stated as follows:

The volume of a given mass of gas increases or decreases by $1/273$ of its volume at 0°C for each degree rise or fall of temperature, provided pressure and mass is kept constant.

Thus, if the volumes of a gas at 0°C and $t^\circ\text{C}$ are V_0 and V_t , respectively, then

$$V_t = V_0 + \frac{t}{273.15} V_0 = V_0 \left(1 + \frac{t}{273.15} \right) = V_0 \left(\frac{273.15 + t}{273.15} \right)$$

At this stage, we define a new scale of temperature such that $t^\circ\text{C}$ on the new scale is given by $T = 273.15 + t$ and 0°C is given by $T_0 = 273.15$. This new temperature scale is called the *Kelvin temperature scale* or *absolute temperature scale*.

Absolute scale of temperature: By carrying out similar calculations, it can be shown that the volume of the gas below 0°C will be less than V_0 . For example, the volume of the gas at $-t^\circ\text{C}$ is given by

$$V_{-t} = V_0 \left(1 - \frac{t}{273} \right)$$

Thus, a decrease in temperature results in a decrease in the volume of the gas, and ultimately the volume becomes zero at -273°C . It means that any further lowering of temperature is impossible because it will correspond to negative volume, which is meaningless. Hence, an important conclusion can be drawn from the above discussion that the lowest possible temperature is -273°C . This lowest possible temperature at which all gases are supposed to occupy zero volume is called *absolute zero*. A scale of temperature based upon this choice of zero is called *absolute scale of temperature*. Since this scale was suggested by British scientist Lord Kelvin, it is also known after his name as *Kelvin scale of temperature*.

Careful measurements have revealed that the absolute zero of temperature is -273.15°C . Temperatures in Kelvin are indicated by writing the letter K. By convention, the degree sign ($^\circ$) is not used in expressing temperatures in Kelvin. For example, $-273.15^\circ\text{C} = 0 \text{ K}$

The relationship between Kelvin and Celsius scales is $T = t + 273.15$

where T is the temperature in Kelvin and t is the temperature in the Celsius. While solving numerical problems, a temperature in Celsius scale is converted into Kelvin scale by adding 273 instead of 273.15 for the sake of simplicity.

It is worthwhile to mention here that our conclusion that gases occupy zero volume at 0 K cannot be realised in actual practice because all gases condense to liquids and solids before this temperature is reached. However, the Kelvin scale is quite significant for scientific work and can be justified by thermodynamic arguments. For this reason, it is sometimes called the *thermodynamic scale of temperature*.

Alternative statement of Charles' law: We have already derived the relationship between the volume of a given mass of gas at $t^\circ\text{C}$ (V_t) and that at 0°C (V_0).

$$V_t = V_0 \left(1 + \frac{t}{273} \right) = V_0 \left(\frac{273 + t}{273} \right) = V_0 \frac{T_t}{T_0}$$

where T is the corresponding temperature on the Kelvin scale.

$$\frac{V_t}{T_t} = \frac{V_0}{T_0}$$

$$\therefore \frac{V}{T} = \text{constant (at constant } P \text{ and } n)$$

or $V \propto T$ (at constant P and n)

$$\Rightarrow V = KT$$

Here K is a constant whose value depends upon the pressure of the gas, the amount of the gas, and the units of volume (V).

Thus, Charles' law may be stated in an alternate way as follows:

The volume of a given mass of gas at constant pressure is directly proportional to its temperature on the Kelvin Scale.

Let V_1 be the volume of a certain mass of gas at temperature T_1 and pressure P . If the temperature is changed to T_2 keeping pressure constant, the volume changes to V_2 . The relationship among the four variables V_1 , T_1 , V_2 , and T_2 is

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ (pressure and mass constant)}$$

The law can be experimentally verified by measuring the volumes of the given mass of gas at different temperatures keeping the pressure constant. In each case, the ratio V/T is found to be constant.

The volume-temperature data for 1 mol of N_2 at 1 bar pressure is given in Table 5.3.

Table 5.3 Volume-temperature data for N_2 at 1 bar pressure

Temperature		Volume (dm ³)	V/T
0°C (T)	K(T)		
-50	223.15	18.52	0.083
0	273.15	22.67	0.083
50	323.15	26.82	0.083
100	373.15	30.97	0.083
150	423.15	35.12	0.083

GRAPHICAL REPRESENTATION OF CHARLES' LAW

Charles found that for all gases, at any given pressure, the graph of volume versus temperature (in Celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at -273.15°C . The slopes of lines obtained at different pressure are different, but at zero volume, all lines meet the temperature axis at -273.15°C [Fig. 5.13(a)].

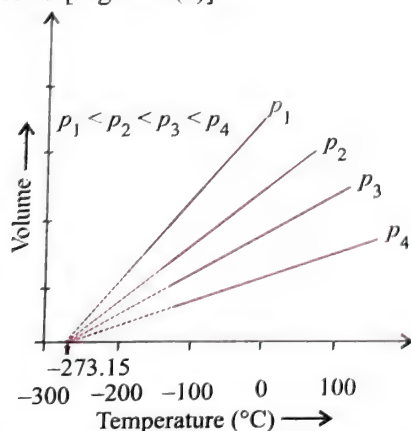


Fig. 5.13(a) Volume vs temperature ($^\circ\text{C}$) graph

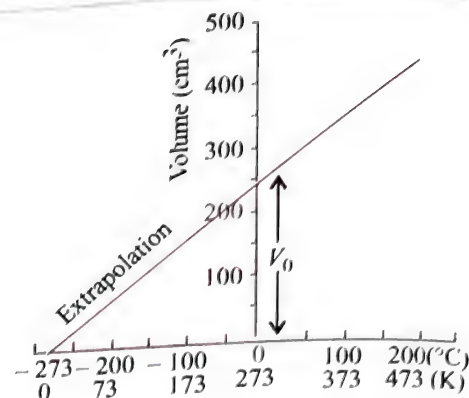


Fig. 5.13(b) A plot of volume versus temperature

Each line in the volume versus temperature graph is called an *isobar*.

We can see that the volume of a gas at -273.15°C will be zero. This means that the gas will not exist. In fact all gases get liquefied before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called *absolute zero*.

Fig. 5.14 shows some more graphical representations verifying Charles law.

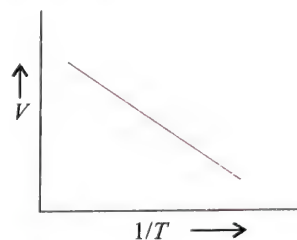


Fig. 5.14(a) Plot of V vs $1/T$

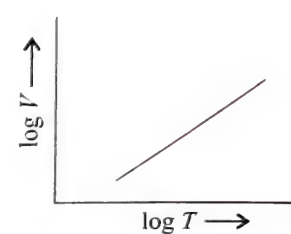


Fig. 5.14(b) Plot of $\log V$ vs $\log T$

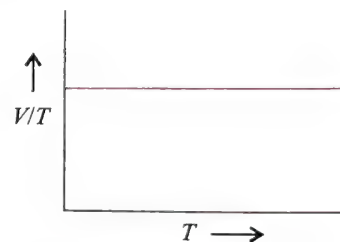


Fig. 5.14(c) Plot of V/T vs T

PRACTICAL IMPORTANCE OF CHARLES' LAW

The use of hot air balloons in sports and for meteorological observations is an interesting application of Charles' law. According to Charles' law, gases expand on heating. Since the mass of a gas is unchanged, larger volume corresponds to lower density. Thus, hot air is less dense than cold air. This causes hot air balloons to rise by displacing cooler air of the atmosphere.

All gases obey Charles' law at very low pressure and high temperature.

ILLUSTRATION 5.11

A gas at 300 K is compressed to reduce its volume to half of its volume. At what temperature, will it become double of its initial volume?

Sol. Let initial volume $V_1 = V$ at 300 K

Final volume $V_2 = \frac{V}{2}$ at T_2 temperature

Then according to Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore T_2 = \frac{V_2 \times T_1}{V_1} = \frac{\frac{V}{2} \times 300}{\frac{V}{2}} = 150 \text{ K}$$

Hence, the final temperature is 150 K.

ILLUSTRATION 5.12

On a ship sailing in Pacific ocean where temperature is 23.4°C , a balloon is filled with 2 L air. What will be the volume of balloon when the ship reaches Indian ocean where temperature is 26.1°C .

Sol. According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 2 \text{ L}, V_2 = ?$$

$$T_1 = 273 + 23.4 = 296.4 \text{ K}$$

$$T_2 = 273 + 26.1 = 299.1 \text{ K}$$

$$\therefore V_2 = \frac{V_1 \times T_2}{T_1} = \frac{2 \text{ L} \times 299.1 \text{ K}}{296.4 \text{ K}} = 2.01842 \text{ L}$$

ILLUSTRATION 5.13

At what temperature, the volume of a given amount of gas at 25°C becomes twice when pressure is kept constant?

Sol. Let the initial volume of gas be $V_1 = V$.

The final volume of gas (V_2) is $2V$.

$$T_1 = 273 + 25 = 298 \text{ K}$$

$$T_2 = ?$$

According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore T_2 = \frac{V_2 \times T_1}{V_1} = \frac{2V \times 298}{V} = 596 \text{ K}$$

Therefore, the final temperature would be 596 K.

ILLUSTRATION 5.14

An open flask contains air at 27°C . To what temperature it must be heated to expel one-fourth of the air?

Sol. Let volume of flask = 1 L

Volume \propto number of moles initially (n_1)

$$\text{Volume of air expelled } \frac{1}{4} \text{ L} \propto \frac{1}{4} n_1$$

Number of moles left in the flask

$$= \left(n_1 - \frac{1}{4} n_1 \right) = \frac{3}{4} n_1$$

Ideal gas equation:

$$P_1 V_1 = n_1 R T_1 \quad \dots(i), \quad P_1 V_1 = n_2 R T_2 \quad \dots(ii)$$

(Since P and V of the flask is constant)

From Eqs. (i) and (ii)

$$\therefore n_1 T_1 = n_2 T_2$$

$$n_1 \times 300 = \frac{3}{4} n_1 T_2$$

$$T_2 = 300 \times \frac{4}{3} = 400 \text{ K} = 127^\circ\text{C}$$

ILLUSTRATION 5.15

flask having a volume of 250.0 mL and containing air is heated to 100°C and sealed. Then the flask is cooled to 25°C , immersed in water, and opened. What volume of water will be drawn back into the flask, assuming the pressure remaining constant?

Sol. Let the volume (V_1) of the flask be 250.0 mL

at temperature (T_1) = $100 + 273 = 373 \text{ K}$

Flask cooled to temperature (T_2) = $25 + 273 = 298 \text{ K}$

According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Hence, the volume (V_2) at 298 K is $\frac{V_1 \times T_2}{T_1}$.

$$\therefore V_2 = \frac{250 \times 298}{373} = 199.73 \text{ cm}^3$$

Therefore, water drawn back is $250 - 199.73 = 50.27 \text{ cm}^3$

ILLUSTRATION 5.16

The volume expansivity of a gas under constant pressure is 0.0037 or $\left(\frac{1}{273} \right)$. Calculate its volume at -100°C if its volume at 100°C is 685 cm^3 .

Sol. The volume expansivity of a gas means increase or decrease in volume per degree rise or fall in temperature of its volume at 0°C . Therefore,

$$V_t = V_0 + 0.0037 \times V_0 \times t = V_0(1 + 0.0037t)$$

$$\text{At } 100^\circ\text{C}, V_{100^\circ\text{C}} = V_0(1 + 0.0037 \times 100) = 685 \text{ cm}^3$$

Solve for V_0 :

$$\therefore V_0 = \frac{685}{1.37} = 500 \text{ cm}^3$$

Therefore, volume at -100°C is

$$V_{-100^\circ\text{C}} = V_0[1 + 0.0037 \times (-100)]$$

$$= 500[1 + 0.0037 \times (-100)] = 315 \text{ cm}^3$$

Hence, volume at -100°C is $V_{-100} = 315 \text{ cm}^3$.

ILLUSTRATION 5.17

In terms of Charles' law, explain why -273°C is the lowest possible temperature?

Sol. The temperature -273°C (or 0 K) is known as the absolute zero temperature. Below this temperature, a substance cannot exist as gas and changes to liquid. This means that Charles' law can be applied only up to a temperature of -273°C , since a substance fails to exist as gas below this temperature.

ILLUSTRATION 5.18

A sample of gas is found to occupy a volume of 900 cm^3 at 27°C . Calculate the temperature at which it will occupy a volume of 300 cm^3 , provided the pressure is kept constant.

Sol. Here, $V_1 = 900 \text{ cm}^3$, $V_2 = 300 \text{ cm}^3$

$$T_1 = (27 + 273) \text{ K} = 300 \text{ K}, T_2 = ?$$

Applying Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore T_2 = \frac{V_2 T_1}{V_1} = \frac{300 \text{ cm}^3 \times 300 \text{ K}}{900 \text{ cm}^3} = 100 \text{ K}$$

$$= 100 - 273 = -173^\circ\text{C}$$

ILLUSTRATION 5.19

It is desired to increase the volume of 80 cm^3 of a gas by 20% without changing pressure. To what temperature the gas be heated if its initial temperature is 25°C ?

Sol. The desired increase in the volume of gas is

$$20\% \text{ of } 80 \text{ cm}^3 = \frac{80}{100} \times 20 = 16 \text{ cm}^3$$

Thus, the final volume of the gas is $80 + 16 = 96 \text{ cm}^3$.

$$\text{Now, } V_1 = 80 \text{ cm}^3, V_2 = 96 \text{ cm}^3$$

$$T_1 = 25^\circ\text{C} = 298 \text{ K}, T_2 = ?$$

Applying Charles' law, we get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore T_2 = \frac{V_2 T_1}{V_1} = \frac{96 \text{ cm}^3 \times 298 \text{ K}}{80 \text{ cm}^3} = 357.6 \text{ K}$$

$$= 357.6 - 273 = 83.4^\circ\text{C}$$

It states that the pressure of a given mass of gas is directly proportional to the Kelvin temperature at constant volume.

Mathematically, $P \propto T$ (at constant n and V)

$$\text{or } \frac{P}{T} = K \text{ (constant)}$$

The value of K depends upon the volume of the gas, the amount of the gas, and the units of pressure (P).

Let P_1 be the pressure of a certain mass of gas at temperature T_1 and volume V . If the temperature is changed to T_2 at the same volume so that the corresponding pressure becomes P_2 , then according to the law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ (at constant } n \text{ and } V)$$

The above relationship can be derived from Boyle's law and Charles law. The plot of pressure versus temperature (K) for a fixed mass of gas at constant volume is a straight line as shown in Fig. 5.15. Each line in this plot is called an *isochore*.

The slopes of various isochores at different volumes are different, but all these lines meet the temperature axis on extrapolation at 0 (K) as shown is Fig. 5.15.

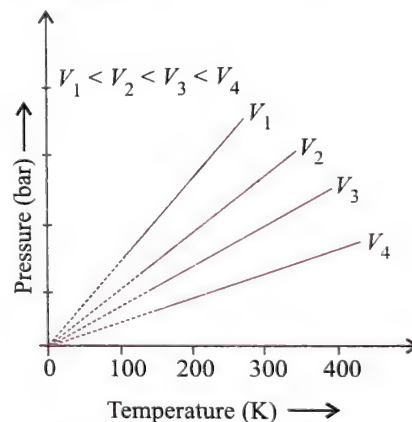


Fig. 5.15 Pressure versus temperature (K) graph (isochores) of a gas

Fig. 5.16 shows different graphical representations of Gay-Lussac's law

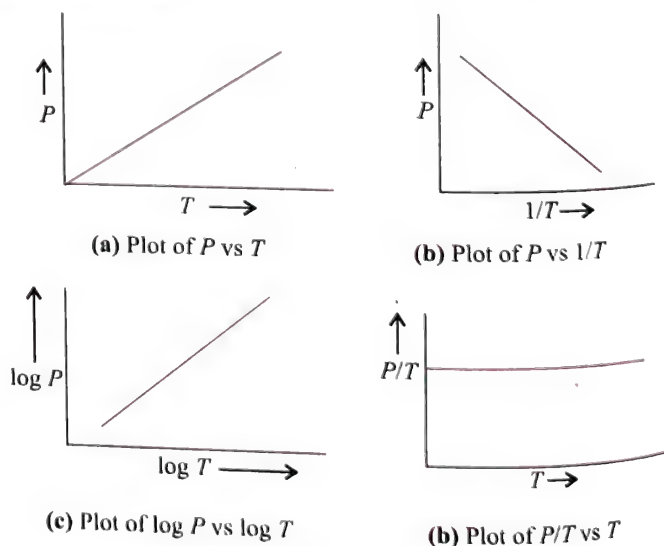


Fig. 5.16

5.6.3 GAY-LUSSAC'S LAW (PRESSURE-TEMPERATURE RELATIONSHIP)

This law is similar to Charles' law and is given by Joseph Gay-Lussac. It describes the pressure-temperature relationship of gases at constant volume. It is also called Amonton's law.

ILLUSTRATION 5.20

A cylinder containing cooking gas can withstand a pressure of 15 atm. The pressure gauge of the cylinder indicates 12 atm at 27°C. Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode?

Sol. Given, $P_1 = 15$ atm, $T_2 = ?$

$$P_2 = 12 \text{ atm}, T_2 = 300 \text{ K} (273 + 27)$$

Since the volume of the cylinder remains constant,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\therefore \frac{15}{T_1} = \frac{12}{300}$$

$$T_1 = 375 \text{ K}$$

i.e., the cylinder will explode above 375 K or 102°C.

ILLUSTRATION 5.21

An iron tank contains helium at a pressure of 2 atm at 25°C. The tank can withstand a maximum pressure of 10 atm. The building in which the tank has been placed catches fire. Predict whether the tank will blow up first or melt. (The melting point of iron is 2235 K).

Sol. Let $P_1 = 2$ atm, $P_2 = ?$

$$T_1 = 25^\circ\text{C} = 298 \text{ K}, T_2 = 2235 \text{ K}$$

According to Gay Lussac's equation,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\text{Thus, } P_2 = \frac{P_1 T_2}{T_1} = \frac{2 \times 2235}{298} = 15 \text{ atm}$$

Since the pressure of the gas in the tank is more than 10 atm at the melting point, this tank will blow up before reaching the melting point.

ILLUSTRATION 5.22

A steel tank contains air at a pressure of 15 bar at 20°C. The tank is provided with a safety valve which can withstand a pressure of 30 bar. Calculate the temperature to which the tank can be safely heated.

Sol. Let $P_1 = 15$ bar, $P_2 = 30$ bar

$$T_1 = 20^\circ\text{C} = 293 \text{ K}, T_2 = ?$$

$$\text{Now, } \frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ or } T_2 = \frac{P_2 T_1}{P_1} = \frac{30 \times 293}{15}$$

$$\therefore T_2 = 586 \text{ K or } 313^\circ\text{C}$$

Thus, the safety valve will blow up when the temperature exceeds 313°C.

ILLUSTRATION 5.23

A balloon blown up at 5°C has a volume of 480 mL. At this stage, the balloon is distended to 7/8 of its maximum stretching capacity.

- Will the balloon burst if it is brought to a room having temperature 30°C?
- Calculate the temperature at which the balloon will burst.

Sol. 480 mL represents 7/8 of the balloon's maximum capacity.

Let x mL is the maximum volume capacity of the balloon

$$\therefore \frac{7}{8}x = 480 \text{ mL}$$

$$x = \frac{480 \times 8}{7} = 548.6 \text{ mL}$$

Thus, if volume exceeds 548.6 mL, the balloon will burst.

- Calculation of the volume of balloon at 30°C:

By Charles' law, we get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\text{Here, } V_1 = 480 \text{ mL}, V_2 = ? T_1 = 278 \text{ K}, T_2 = 303 \text{ K}$$

$$\text{Thus, } V_2 = \frac{V_1 T_2}{T_1} = \frac{480 \times 303}{278} = 523.16 \text{ mL}$$

Therefore, the balloon will not burst at 30°C.

- Calculation of the temperature at which balloon will burst:

$$\text{Here, } V_1 = 480 \text{ mL}, T_2 = 278 \text{ K}, V_2 = 548.6 \text{ mL}, T_2 = ?$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore T_2 = \frac{V_2 \times T_1}{V_1} = \frac{548.6 \times 278}{480} = 317.7 \text{ K}$$

$$= 317.7 - 273 = 44.7^\circ\text{C}$$

Thus the balloon will burst as soon as temperature exceeds 44.7°C.

ILLUSTRATION 5.24

20 mL of hydrogen measured at 15°C is heated to 35°C. What is the new volume at the same pressure?

Sol. Given conditions

Final conditions

$$V_1 = 20 \text{ mL}$$

$$V_2 = ? \text{ mL}$$

$$T_1 = 15 + 273 = 288 \text{ K}$$

$$T_2 = 35 + 273 = 308 \text{ K}$$

By applying Charles' law, we get

$$\frac{V_2}{308} = \frac{20}{288}$$

$$V_2 = \frac{20}{288} \times 308 = 21.38$$

The volume of hydrogen gas at 35°C is 21.38 mL.

ILLUSTRATION 5.25

At what temperature in centigrade will the volume of a gas at 0°C double itself, pressure remaining constant?

Sol. Let the volume of the gas at 0°C be V mL

Thus, we have

$$V_1 = V \text{ mL}, V_2 = 2V \text{ mL}$$

$$T_1 = 0 + 273 = 273 \text{ K}, T_2 = ?$$

By applying Charles' law, we get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Substituting the corresponding values, we have

$$\frac{V}{273} = \frac{2V}{T_2}$$

$$T_2 = \frac{2V \times 273}{V} = 546 \text{ K} = 546 - 273 = 273^\circ\text{C}$$

ILLUSTRATION 5.26

A 10.0 L container is filled with a gas to a pressure of 2.00 atm at 0°C . At what temperature will the pressure inside the container be 2.50 atm?

Sol. As the volume of the container remains constant, applying pressure-temperature law, viz.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

We get

$$\frac{2 \text{ atm}}{273 \text{ K}} = \frac{2.50 \text{ atm}}{T_2}$$

$$\text{or } T_2 = 341 \text{ K} = 341 - 273^\circ\text{C} = 68^\circ\text{C}$$

ILLUSTRATION 5.27

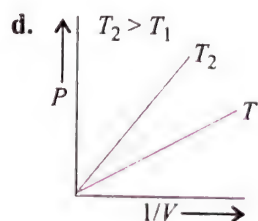
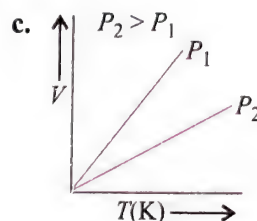
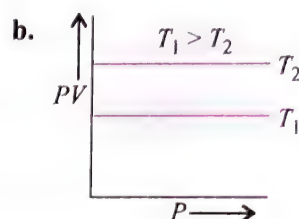
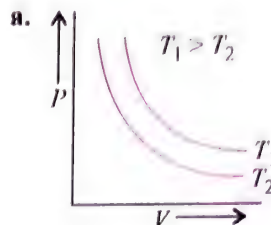
- I. Two flasks A and B have equal volumes. A is maintained at 300 K and B at 600 K. While A contains H_2 gas, B has an equal mass of CH_4 gas. Assuming ideal behaviour for both the gases. Which is true about number of molecules in A and B

- Flask A contains eight times more molecules than flask B.
- Flask B contains eight times more molecules than flask A.
- Both flasks contain an equal number of molecules.
- Flask A contains four times more molecules than flask B.

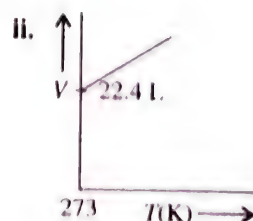
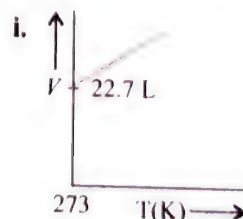
- II. Which of the following is true about pressures in flasks A and B?

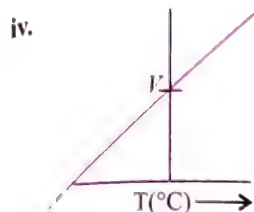
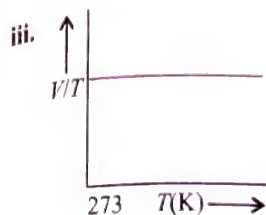
- The pressure in flask A is four times that in flask B.
- The pressure in flask B is four times that in flask A.
- Both flasks have same pressure.
- The pressure in flask A is eight times that in flask B.

- III. Which of the following graphs is consistent with ideal gas behaviour?



- IV. For a fixed mass of gas and constant pressure, which of the following graphs is/are correct?



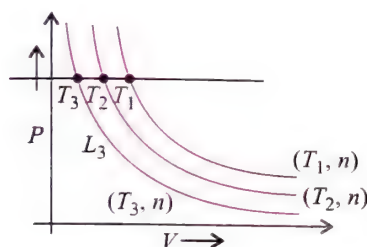


The correct choice is:

- a. I b. I, II, IV
c. I, II, III d. II, III, IV

- v. Boyle's Law for an ideal gas can be plotted as shown (\rightarrow)
(n : moles; T : temperature)

Note: T and n are kept constant along line L_1 , L_2 , and L_3 .



It follows from the above graph:

- a. $T_1 > T_2 > T_3$
b. $T_1 < T_2 < T_3$
c. $T_1 = T_2 = T_3$
d. None of these

Sol.

I. a. $n_A = \frac{m}{2}, n_B = \frac{m}{16}, \frac{n_A}{n_B} = 8$

since $n_A \propto N, \therefore \frac{N_A}{N_B} = 8$

(n = number of moles) (N = number of molecules)

II. a. $P_A V = n_A R T_A; P_B V = n_B R T_B$

$$\frac{P_A}{P_B} = \frac{n_A T_A}{n_B T_B} = 8 \times \frac{300}{600} = 4$$

$$n_A = \frac{m}{2}, n_B = \frac{m}{16}, \frac{n_A}{n_B} = 8$$

III. a. $T_1 > T_2$

IV. d.

V. a. $T_1 > T_2 > T_3$

5.6.4 AVOGADRO'S LAW (VOLUME-AMOUNT RELATIONSHIP)

This law relates the volume of a gas to the number of molecules at constant temperature and pressure. It was given by Amadeo Avogadro in 1811. It states that *equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.*

This means that as long as the temperature and pressure remain constant, the volume depends upon the number of molecules of the gas or amount of the gas.

For example, 1 mol of all gases contains 6.023×10^{23} molecules. At the same time, moles of all gases at 273.15 K (0°C) and 1 bar pressure occupy a volume of 22.7 L ($22.7 \times 10^{-3} \text{ m}^3$). Therefore, the volume of the gas is directly proportional to the number of molecules.

Mathematically we can write

$$V \propto N \text{ (temperature and pressure constant)}$$

The number of molecules (N) of any gas is directly proportional to its number of moles (n). Thus

$$V \propto n \text{ (temperature and pressure constant)}$$

$$\text{or } V = Kn, K \text{ is the constant of proportionality}$$

The number of molecules in 1 mol of a gas has been determined to be 6.022×10^{23} and is known as *Avogadro's constant*.

Molar volume of some gases is given in Table 5.4.

Table 5.4 Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP)

Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

If m is the mass of a gas having molar mass M , then the number of moles of a gas can be calculated as follows:

$$n = \frac{m}{M} \quad \dots(i)$$

$$\text{Thus, } V = k \frac{m}{M} \quad \dots(ii)$$

$$\text{or } M = k \frac{m}{V} = k \cdot d \quad \dots(iii)$$

where d is the density of the gas.

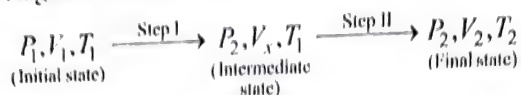
Thus, we can conclude that the density of a gas is directly proportional to its molar mass.

5.7 IDEAL GAS

A gas that follows Boyle's law, Charles' law, and Avogadro's law strictly is called an *ideal gas*. Such a gas is hypothetical. It is assumed that intermolecular forces are not present between the molecules of an ideal gas. Real gases follow these laws only under certain specific conditions when the forces of interaction are practically negligible, i.e., at low pressure and very high temperature. In all other situations, they deviate from ideal behaviour. You will learn about the deviations later in this unit.

5.7.1 DERIVATION OF IDEAL GAS EQUATION

We have studied different gas laws in the previous sections. The combination of these laws, namely, Boyle's law, Charles' law, and Avogadro's law, leads to the development of an equation that relates four variables; pressure, volume, absolute temperature, and number of moles. The equation so formulated is called the *gas equation*. In order to develop the gas equation, let us consider a certain quantity of gas occupying a volume V_1 at temperature T_1 and pressure P_1 . Let the pressure and temperature be changed to P_2 and T_2 , respectively, so that the volume changes to V_2 . Suppose that this change from the initial state has been brought about in two stages as shown below:



In Step I, T is constant; therefore, Boyle's law is applicable.

$$P_1 V_1 = P_2 V_x \Rightarrow V_x = \frac{P_1 V_1}{P_2}$$

In Step II, P is constant; therefore, Charles' law is applicable.

$$\frac{V_x}{T_1} = \frac{V_2}{T_2} \Rightarrow V_x = \frac{V_2 T_1}{T_2}$$

Equating the two values of V_x , we get

$$\frac{P_1 V_1}{P_2} = \frac{V_2 T_1}{T_2}$$

$$\text{or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This equation is quite useful for calculating one of the variables if the values of other variables are known. This equation is also known as the combined gas law.

Another important conclusion that can be drawn from the equation is that the ratio of PV to the absolute temperature T for a given quantity of gas is constant. That is

$$\frac{PV}{T} = \text{constant} = K$$

The value of K depends upon the amount of the gas. In order to make the equation independent of the amount of the gas, we take the help of Avogadro's law according to which the volume of the gas at constant temperature and pressure is proportional to its number of moles (n). This means that K is directly proportional to the number of moles (n). Thus,

$$K \propto n \text{ or } K = nR$$

where R is the constant of proportionality, which is independent of the amount as well as nature of the gas and is known as *universal gas constant*. It leads to the conclusion that

$$\frac{PV}{T} = nR$$

$$\text{or } PV = nRT$$

This equation relates the four variables P , V , T , and n and is called the *ideal gas equation*.

Alternative derivation of ideal gas equation: The gas equation can also be derived by combining Boyle's law, Charles' law, and Avogadro's law as follows:

According to Boyle's law

$$V \propto \frac{1}{P} \text{ (at constant } T \text{ and } n) \quad \dots (i)$$

According to Charles' law,

$$V \propto T \text{ (at constant } P \text{ and } n) \quad \dots (ii)$$

According to Avogadro's law,

$$V \propto n \text{ (at constant } T \text{ and } P) \quad \dots (iii)$$

Combining equations (i), (ii), and (iii), we get

$$V \propto \frac{nT}{P}$$

$$\text{or } PV \propto nT \text{ or } PV = nRT$$

where R is the constant of proportionality and is known as the *universal gas constant*.

The ideal gas equation is a relation among four variables and describes the state of any gas. Therefore, it is also called the *equation of state*.

Nature of the gas constant (R): In order to understand the significance of R , let us examine the nature of quantities in the ideal gas equation.

$$PV = nRT$$

$$\text{or } R = \frac{PV}{nT}$$

$$\text{i.e., } R = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Temperature}}$$

Now, pressure is force per unit area. So

$$R = \frac{(\text{Force/Area}) \times \text{Volume}}{\text{Moles} \times \text{Temperature}}$$

$$= \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Moles} \times \text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Temperature}}$$

Since, force \times Length = Work energy

$$\therefore R = \frac{\text{Work}}{\text{Moles} \times \text{Temperature}}$$

Thus, R represents work done per Kelvin per mole. Since work can be expressed in different systems of units, R will have different numerical values in different systems.

Numerical value of R : The numerical value of R depends upon the units in which pressure and volume are expressed. Let us calculate the value of R when pressure and volume are expressed in different units.

- a. In SI unit, pressure is expressed in N m^{-2} and volume in m^3 . Then the numerical value of R in SI units can be calculated as follows:

From the general gas equation, we get

$$R = \frac{PV}{nT}$$

Substituting the values for 1 mol of gas at STP, we get

$$\begin{aligned} R &= \frac{(101325 \text{ N m}^{-2})(22.4 \times 10^{-3} \text{ m}^3)}{(1 \text{ mol})(273.15 \text{ K})} \\ &= 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

- b. When pressure is expressed in atmosphere and volume in litres, the value of R comes out to be in litre-atmosphere per degree per mole.

Substituting these values for 1 mol of gas at STP, we get

$$R = \frac{1(\text{atm}) \times 22.4 (\text{L})}{(1 \text{ mol}) \times 273.3 (\text{K})} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

- c. When pressure is expressed in bar and volume in dm^3 , we know that 1 mol of any gas at 1 bar pressure and 273.15 K occupies a volume of 22.7 dm^3 or 22.7 L. Then,

$$R = \frac{1(\text{bar}) \times 22.7 (\text{L})}{(1 \text{ mol}) \times 273.15 (\text{K})} = 0.0831 \text{ bar L K}^{-1} \text{ mol}^{-1}$$

- d. In CGS units, when pressure is expressed in dynes per square centimetre and volume in cubic centimetre, then R has the units erg per degree per mole or calories per degree per mole. For 1 mol of a gas at STP, we have

$P = 76 \text{ cm}$ length of Hg column ($P = \text{hdg}$)

$$1 \text{ atm} = (76 \text{ cm}) (13.596 \text{ g cm}^{-3}) \times 980.6 \text{ cm s}^{-2}$$

$$= 1013250 \text{ g cm}^{-1} \text{ s}^{-2}$$

$$= 1013250 \text{ dyn cm}^{-2}$$

$$\text{Density of mercury} = 13.596 \text{ g cm}^{-3}$$

$$g = 980.6 \text{ cm s}^{-2}$$

$$V = 22400 \text{ cm}^3$$

$$T = 273.15 \text{ K}$$

$$\therefore R = \frac{(1013250 \text{ dyn cm}^{-2}) (22400 \text{ cm}^3)}{(1 \text{ mol}) (273.15 \text{ K})}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

Further, we know that

$$4.184 \times 10^7 \text{ erg} = 1 \text{ cal}$$

$$\therefore R = \frac{8.314 \times 10^7}{4.183 \times 10^7} = 1.99 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\text{or } R \approx 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

It may be noted that although R can be expressed in different units, for pressure-volume calculations, R must be taken in the same units as those used for pressure and volume.

The values of R in different units have been listed in Table 5.5.

Table 5.5 Values of R in different units

Values of R	Units of P	Units of V
0.0821 L atm K ⁻¹ mol ⁻¹	atm	L
0.0831 bar L K ⁻¹ mol ⁻¹	bar	L
62.3 L mm K ⁻¹ mol ⁻¹	mm	L
8.31×10^7 erg K ⁻¹ mol ⁻¹	dynes cm ⁻²	cm ³
8.31 J K ⁻¹ mol ⁻¹	Pa or N m ⁻²	cm ³
1.99 cal K ⁻¹ mol ⁻¹	dyn cm ⁻²	cm ³
8.31 kPa dm ³ K ⁻¹ mol ⁻¹	kPa	dm ³

Standard temperature and pressure (STP): Since the volume of a given mass of gas depends on temperature and pressure, it is necessary to specify the values of P and T when the value of V is stated. In general, the comparison of the volumes of different gases is made with reference to standard temperature

and pressure. For gases, the standard temperature is taken as 0°C (273.15 K) and standard pressure as 1 atm (101.325 kPa) or 760 mm Hg. The conditions are abbreviated as STP, meaning standard temperature and pressure or NTP, meaning normal temperature and pressure.

In brief, STP refers to

Temperature = 0°C or 273.15 K

Pressure = 1 atm or 760 mm Hg or 760 torr or 101.325 kPa

- a. STP (Standard temperature and pressure) or NTP (normal temperature and pressure) conditions are $T = 0^\circ\text{C} = 273.15 \text{ K}$, $P = 1 \text{ atm}$

or

$$T = 0^\circ\text{C} = 273.15 \text{ K}, \quad P = 1 \text{ bar}$$

- i. Volume of a gas at STP ($P = 1 \text{ atm}$)

$$= 22.413996 \text{ L mol}^{-1} \approx 22.4 \text{ L mol}^{-1}$$

- ii. Volume of a gas at STP ($P = 1 \text{ bar}$)

$$= 22.71098 \text{ L mol}^{-1} \approx 22.7 \text{ L mol}^{-1}$$

- b. SATP (standard ambient temperature and pressure) or standard conditions are:

- i. $T = 25^\circ\text{C} = 298.15 \text{ K}$, $P = 1 \text{ atm}$

or

- ii. $T = 25^\circ\text{C} = 298.15 \text{ K}$, $P = 1 \text{ bar}$ (10^5 Pa)

- iii. Volume of a gas at SATP (or standard conditions) when ($P = 1 \text{ atm}$) = 24.4 L mol^{-1} .

- iv. Volume of a gas at SATP (or standard conditions) when ($P = 1 \text{ bar}$) = $24.789 \text{ L mol}^{-1}$
= 24.7 L mol^{-1}

5.7.2 DENSITY AND MOLAR MASS OF A GASEOUS SUBSTANCE

We have studied in chapter one that the number of moles of a substance is related to its molar mass as

$$n = \frac{w}{M}$$

where n is the number of moles, w is the mass in gram, and M is the molar mass.

Substituting this value in the ideal gas equation, we can get the relationship between density and molar mass.

$$PV = nRT = \frac{w}{Mw} RT$$

$$P = \frac{wRT}{Mw} = \frac{dRT}{Mw}$$

$$\text{where } d \text{ is the density of gas } \left[d = \frac{\text{Mass}}{\text{Volume}} = \frac{w}{V} \right]$$

$$Mw = \frac{dRT}{P}$$

ILLUSTRATION 5.28

A sample of nitrogen occupies a volume of 320 cm^3 at STP. Calculate its volume at 546.3 K and 0.5 bar pressure.

Sol. Given, $P_1 = 1.0 \text{ bar}$, $P_2 = 0.5 \text{ bar}$

$$V_1 = 320 \text{ cm}^3, V_2 = ?$$

$$T_1 = 273.15 \text{ K}, T_2 = 546.3 \text{ K}$$

According to gas equation, we get

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore V_2 = \frac{P_1 V_1 \times T_2}{T_1 \times P_2} = \frac{1 \times 320 \times 546.3}{273.15 \times 0.5} = 1280 \text{ cm}^3$$

ILLUSTRATION 5.29

1.0 mol of pure dinitrogen gas at SATP conditions was put into a vessel of volume 24.8 m^3 maintained at the temperature of 596.3 K . What is the pressure of the gas in the vessel?

Sol. Volume of 1.0 mol of a gas at SATP (V_1) = $24.8 \times 10^{-3} \text{ m}^3$

Initial condition (SATP) Final condition

$$V_1 = 24.8 \times 10^{-3} \text{ m}^3 \quad V_2 = 24.8 \text{ m}^3$$

$$P_1 = 1 \text{ bar} \quad P_2 = ?$$

$$T_1 = 298.15 \text{ K} \quad T_2 = 596.3 \text{ K}$$

According to the gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } P_2 = \frac{P_1 V_1 \times T_2}{T_1 \times V_2} = \frac{1.0 \times 24.8 \times 10^{-3} \times 596.3}{298.15 \times 24.8} = 2 \times 10^{-3} \text{ bar}$$

$$\therefore P_2 = 2 \times 10^{-3} \text{ bar}$$

ILLUSTRATION 5.30

A sample of gas occupies a volume of 320 cm^3 at STP. Calculate its volume at 66°C and 0.825 atm pressure.

Sol. Here,

$$P_1 = 1.00 \text{ atm}, P_2 = 0.825 \text{ atm}$$

$$V_1 = 320 \text{ cm}^3, V_2 = ?$$

$$T_1 = 273 \text{ K},$$

$$T_2 = 66^\circ\text{C} = (66 + 273) \text{ K} = 339 \text{ K}$$

According to the gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{1 \times 320 \times 339}{273 \times 0.825} = 482 \text{ cm}^3$$

ILLUSTRATION 5.31

Determine the value of gas constant R when pressure is expressed in Torr and volume in dm^3

Sol. We know,

$$1.01325 \text{ bar} = 760 \text{ Torr. Hence}$$

$$R = \frac{PV}{nT} = \frac{\left\{ 1 \text{ bar} \left(\frac{760 \text{ Torr}}{1.01325 \text{ bar}} \right) \right\} (22.711 \text{ dm}^3)}{(1 \text{ mol})(273.15 \text{ K})} = 62.36 \text{ Torr dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

ILLUSTRATION 5.32

At 25°C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is 640 mL .

Sol. $P_1 = 760 \text{ mm}$ of Hg, $V_1 = 600 \text{ mL}$

$$T_1 = 25 + 273 = 298 \text{ K}, \quad V_2 = 640 \text{ mL}$$

$$T_2 = 10 + 273 = 283 \text{ K},$$

According to combined gas law

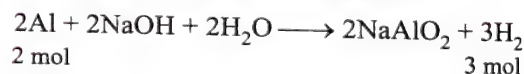
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$$

$$P_2 = \frac{(760 \text{ mm Hg}) \times (600 \text{ mL}) \times (283 \text{ K})}{(298 \text{ K}) \times (640 \text{ mL})} = 676.6 \text{ mm Hg}$$

ILLUSTRATION 5.33

The drain cleaner Drainex contains small bits of aluminium which react with caustic soda to form hydrogen. What volume of hydrogen at 20°C and 1 bar will be released when 0.15 g of aluminium reacts?

Sol. The chemical reaction taking place is



2 mol

3 mol

$$2 \times 27 \text{ g}$$

54 g of Al produces hydrogen = 3 mol

0.15 g of Al produces hydrogen

$$= \frac{3 \times 0.15}{54} \text{ mol} = 8.33 \times 10^{-3} \text{ mol}$$

Calculation of volume of $8.33 \times 10^{-3} \text{ mol}$ of hydrogen at 20°C and 1 bar :

$$V = \frac{nRT}{P} = \frac{8.33 \times 10^{-3} (\text{mol}) \times 0.083 (\text{bar L K}^{-1} \text{mol}^{-1}) \times 293 (\text{K})}{1 (\text{bar})} = 0.20282 \text{ L} = 202.82 \text{ mL}$$

ILLUSTRATION 5.34

The temperature at the foot of a mountain is 30°C and pressure is 760 mm Hg, whereas at the top of the mountain these are 0°C and 710 mm Hg. Compare the densities of air at the foot and top of the mountain.

Sol. Let $P_1 = 760 \text{ mm}$, $T_1 = 30^\circ\text{C} = 303 \text{ K}$, $P_2 = 710 \text{ mm}$, $T_2 = 273 \text{ K}$

We have

$$\rho = \frac{PM}{RT}$$

where ρ is density, M is molar mass, and R is gas constant

Let the density at the top be (ρ_2)

$$\rho_2 = \frac{P_2 M}{RT_2}$$

Let the density at the foot be (ρ_1)

$$\rho_1 = \frac{P_1 M}{RT_1}$$

Hence

$$\frac{\rho_1}{\rho_2} = \frac{P_1}{T_1} \times \frac{T_2}{P_2} = \frac{760}{303} \times \frac{273}{710} = \frac{0.964}{1}$$

$$\therefore \rho_1 : \rho_2 = 0.964 : 1$$

ILLUSTRATION 5.35

The density of a certain gaseous oxide at 1.5 bar pressure and 20°C is same as that of dioxygen at 10°C and 4.5 bar pressure. Calculate the molar mass of the gaseous oxide.

Sol. Density of dioxygen (O_2) at 4.5 bar pressure and 10°C

$$\rho_{O_2} = \frac{PM}{RT} = \frac{4.5 \times 32}{R \times 283.15}$$

$$\rho_{\text{oxide}} = \frac{PM}{RT} = \frac{1.5 \times M}{R \times 293.15}$$

Now, $\rho_{O_2} = \rho_{\text{oxide}}$

$$\therefore \frac{4.5 \times 32}{R \times 283.15} = \frac{1.5 \times M}{R \times 293.15}$$

$$\text{or } M = \frac{4.5 \times 293.15 \times 32}{283.15 \times 1.5} = 99.39 \text{ g mol}^{-1}$$

Therefore, the molecular mass of oxygen dioxide is 99.39 g mol⁻¹.

ILLUSTRATION 5.36

The density of a gas is found to be 5.46 g dm⁻³ at 27°C and 2 bar pressure. What will be its density at STP?

Sol. Let $\rho_1 = 5.46 \text{ g dm}^{-3}$, $P_1 = 2 \text{ bar}$, $T_1 = 27^\circ\text{C} = 300 \text{ K}$

At STP

$$\rho_2 = ?$$

$$P_2 = 1 \text{ bar}$$

$$T_2 = 0^\circ\text{C} = 273.15 \text{ K}$$

Hence,

$$\rho_1 = \frac{P_1 M}{RT_1}; \rho_2 = \frac{P_2 M}{RT_2}$$

$$\text{or } \frac{\rho_1}{\rho_2} = \frac{P_1 T_2}{T_1 P_2} \text{ or } \rho_2 = \frac{\rho_1 T_1 P_2}{P_1 T_2}$$

Substituting the values, we have

$$\rho_2 = \frac{5.46 \times 300 \times 1}{2 \times 273.15} = 3.0 \text{ g dm}^{-3}$$

Hence, density of gas at STP is 3.0 g dm⁻³

ILLUSTRATION 5.37

The density of a gas is found to be 1.56 g L⁻¹ at 745 mm pressure and 60°C. Calculate the molecular mass of the gas.

Sol. We are given

$$\rho = 1.56 \text{ g L}^{-1}$$

$$P = 745 \text{ mm} = \frac{745}{760} \text{ atm}$$

$$T = 60^\circ\text{C} = 60 + 273 = 333 \text{ K}$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$\therefore M = \frac{\rho RT}{P} = \frac{1.56 \times 0.0821 \times 333}{\frac{745}{760}} = 43.5 \text{ amu}$$

The molecular mass of the gas is 43.5 amu.

ILLUSTRATION 5.38

At which of the following four conditions will the density of nitrogen be the largest?

- STP
- 273 K and 2 atm
- 546 K and 1 atm
- 546 K and 2 atm

Sol.

- The density of a gas is given by $\rho = PM/RT$. Obviously, the choice that has a greater P/T will have greater density.

ILLUSTRATION 5.39

Calculate the weight of methane in a 9 L cylinder at 16 atm and 27°C temperature. ($R = 0.08 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

Sol. The ideal gas equation is

$$PV = nRT$$

Given $P = 16 \text{ atm}$, $R = 0.08$, $V = 9 \text{ L}$, $T = 273 + 27^\circ\text{C} = 300 \text{ K}$

Putting these values in the above equation, we get

$$16 \times 9 = n \times 0.08 \times 300$$

$$\therefore \text{Moles } (n) = \frac{16 \times 9}{0.08 \times 300} = 6$$

We know

$$\text{Moles } (n) = \frac{\text{Weight}}{\text{Molecular weight}}$$

$$\begin{aligned} \text{Weight of methane} &= \text{Moles} \times \text{Molecular weight of methane} \\ &= 6 \times 16 \quad (\text{CH}_4 = 12 + 4 = 16) \\ &= 96 \text{ g} \end{aligned}$$

ILLUSTRATION 5.40

Calculate the volume occupied by 5.0 g of acetylene gas at 50°C and 740 mm pressure.

(M_w of $C_2H_2 = 26 \text{ g mol}^{-1}$)

Sol. Weight of acetylene (w) = 5.0 g

Molecular weight of acetylene (C_2H_2);

$$M_{C_2H_2} = 26.0 \text{ g mol}^{-1}$$

\therefore Moles of acetylene

$$n_{C_2H_2} = \frac{w}{M} = \frac{5.0}{26.0} = 0.192$$

$$P = 740 \text{ mm} = \frac{740}{760} \text{ atm}$$

$$T = 273 + 50 = 323 \text{ K}$$

Using the gas equation $PV = nRT$, we get

$$\therefore V = \frac{0.192 \times 0.082 \times 323}{740/760} = 5.23 \text{ L}$$

The volume of acetylene gas is 5.23 L.

ILLUSTRATION 5.41

An open vessel at 27°C is heated until $3/5$ of the air in it is expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.

Sol. Given the vessel is open, its volume remains constant. Therefore, the pressure will also be constant. We have the following two general gas equations:

$$PV = n_1RT_1 \quad \text{and} \quad PV = n_2RT_2$$

where n_1, n_2 are the numbers of moles and T_1, T_2 are the temperatures.

Thus,

$$n_1RT_1 = n_2RT_2$$

$$\text{or } n_1T_1 = n_2T_2$$

Let the initial number of moles be 1.

$$\text{Number of moles remaining} = 1 - \frac{3}{5} = \frac{2}{5} = 0.4$$

$$T_1 = 27 + 273 = 300 \text{ K}, T_2 = ?$$

Putting the values in above equation, we get

$$1 \times 300 = 0.4 \times T_2$$

$$T_2 = \frac{300 \times 1}{0.4} = 750 \text{ K}$$

Thus, the required temperature is $750 - 273 = 477^\circ\text{C}$.

ILLUSTRATION 5.42

What percent of a sample of nitrogen must be allowed to escape if its temperature, pressure, and volume are to be changed from 220°C , 3 atm, and 1.65 L to 110°C , 0.7 atm, and 1 L, respectively?

a. 41.4% b. 8.18%

c. 4.14% d. 81.8%

Sol.

d. Let $P_1 = 3 \text{ atm}$, $T_1 = 220 + 273 = 493 \text{ K}$, $V_1 = 1.65 \text{ L}$
 $P_2 = 0.7 \text{ atm}$, $T_2 = 110 + 273 = 383 \text{ K}$, $V_2 = 1 \text{ L}$

Using the gas $PV = nRT$ equation, we get

$$n_1 = \frac{P_1V_1}{RT_1} \quad \text{and} \quad n_2 = \frac{P_2V_2}{RT_2}$$

Thus, fraction remaining is

$$\frac{n_2}{n_1} = \frac{P_2V_2}{RT_2} \times \frac{RT_1}{P_1V_1} = \frac{0.7 \times 1}{R \times 383} \times \frac{R \times 493}{3 \times 1.65} = 0.182$$

$$\text{Fraction escaped} = 1 - 0.182 = 0.818$$

$$\text{Percentage escaped} = 0.818 \times 100 = 81.8\%$$

So the correct choice is (d).

ILLUSTRATION 5.43

A gas cylinder contains 370 g oxygen at 30.0 atm pressure and 25°C . What mass of oxygen will escape if the cylinder is first heated to 75°C and then the valve is held open until gas pressure becomes 1.0 atm, the temperature being maintained at 75°C ?

Sol. $n = \frac{370}{32} = 11.6 \text{ mol}$

$$V = \frac{nRT}{P} = \frac{11.6 \times 0.082 \times 298}{30.0 \text{ atm}} = 9.432 \text{ L}$$

The final number of moles

$$n = \frac{PV}{RT} = \frac{1.0 \text{ atm} \times 9.43}{0.082 \times 348} = 0.330 \text{ mole}$$

$$\text{Final weight of } O_2 = 0.330 \text{ mol} \times 32 = 10.6 \text{ g}$$

$$\text{Mass of } O_2 \text{ escaped} = 370 \text{ g (initial)} - 10.6 \text{ g (final)} \\ = 359.4 \text{ g}$$

ILLUSTRATION 5.44

A refrigeration tank holding 5.00 L freon gas ($C_2Cl_2F_4$) at 25°C and 3.00 atm pressure developed a leak. When the leak was discovered and repaired, the tank had lost 76.0 g of the gas. What was the pressure of the gas remaining in the tank at 25°C ?

Sol. Original gas pressure

$$n = \frac{PV}{RT} = \frac{3.00 \text{ atm} \times 5.00 \text{ mL}}{0.082 \times 298}$$

$$= 0.613 \text{ mol} = 0.613 \times 171 \text{ g}$$

$$= 105 \text{ g originally present}$$

Quantity remaining

$$105 - 76 = 29 \text{ g} = \frac{29}{171} = 0.17 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{0.17 \times 0.082 \times 298}{5.00 \text{ L}} = 0.83 \text{ atm}$$

ILLUSTRATION 5.45

A quantity of hydrogen gas occupies a volume of 30.0 mL at a certain temperature and pressure. What volume would half of this mass of hydrogen occupy at triple the initial temperature, if the pressure was one-ninth that of the original gas?

Sol. Initial Final
 V 30 mL V_2
 P P_1 $P_2 = 1/9 P_1$
 T T_1 $T_2 = 3 T_1$
 n n_1 $n_2 = 1/2 n_1$
 Using gas equation,
 $pV = nRT$, we get

$$\frac{P_1 V_1}{P_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$$

$$\frac{P_1 \times 30}{\frac{1}{9} P_1 \times V_2} = \frac{n T_1}{\left(\frac{1}{2} n\right) (3 T_1)}$$

$$V_2 = \frac{1}{2} \times 3 \times 9 \times 30.0 = 405 \text{ mL}$$

ILLUSTRATION 5.46

A 10.0 L cylinder of oxygen at 4.0 atm pressure and 17°C developed a leak. When the leak was repaired, 2.50 atm of oxygen remained in the cylinder, still at 17°C. How many moles of gas escaped?

Sol. In original gas pressure; the number of moles is

$$n_1 = \frac{P_1 V}{RT_1} = \frac{4.00 \times 10.0}{0.082 \times 290} = 1.683 \text{ mol}$$

Final moles

$$n_2 = \frac{P_2 V}{RT_2} = \frac{2.50 \times 10.0 \text{ L}}{0.082 \times 290} = 1.05 \text{ mol}$$

$$\text{Moles escaped} = n_2 - n_1 = 1.683 - 1.05 = 0.63 \text{ mol}$$

5.8 DALTON'S LAW OF PARTIAL PRESSURES

In 1807, John Dalton put forward a law describing the relation between the pressure of a mixture of non-reacting gases enclosed in a vessel and their individual pressures. The law states that at constant temperature, the total pressure exerted by a mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases, i.e., the pressures which these gases will exert if they are enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gases is called *partial pressure*.

If P_{total} is the total pressure of the mixture of non-reacting gases at temperature T and volume V and p_1, p_2, p_3, \dots represent the partial pressures of the gases, then mathematically

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots \quad (T \text{ and } V \text{ are constants})$$

The law can be illustrated by considering the following example. Suppose we have three containers of capacity 1 L each; the first contains x moles of nitrogen, the second y moles of oxygen, and the third a mixture of x moles of nitrogen and y moles oxygen. All the three containers are kept at the same temperature.

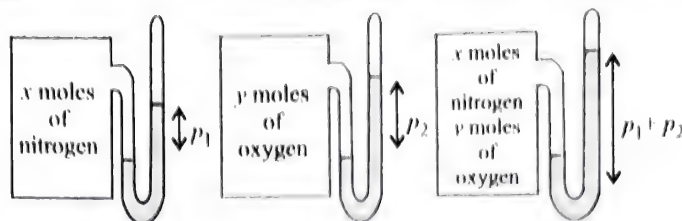


Fig. 5.17 Illustration of Dalton's law of partial pressures

Now if the manometer attached to the first container shows a pressure p_1 and that attached to the second container shows a pressure p_2 , then the pressure in the third container is $p_1 + p_2$.

Utility of Dalton's law: Gases are generally collected over water. Thus they are moist. This law is useful in calculating the pressure of a gas collected by the displacement of water. The gas being collected over water also contains water vapours. The observed pressure of the moist gas is equal to the sum of the pressure of the dry gas and the pressure of the water vapours. The pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas. The pressure of the water vapours is constant at a particular temperature and is known as *aqueous tension* at that temperature. Thus,

$$P_{\text{observed}} = P_{\text{gas}} + \text{Aqueous tension}$$

$$\therefore P_{\text{gas}} = P_{\text{observed}} - \text{Aqueous tension}$$

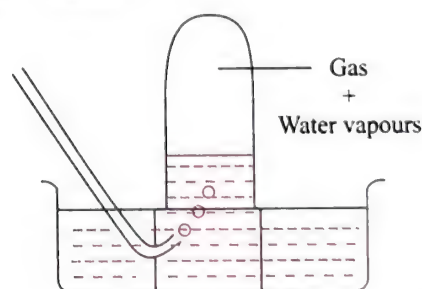


Fig. 5.18 Collection of gas over water

The aqueous tension of water at different temperatures is given in Table 5.6.

Table 5.6 Aqueous tension of water (vapour pressure) as a function of temperature

Temp (K)	Pressure (bar)	Temp (K)	Pressure (bar)
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Partial pressure in terms of mole fraction: Suppose at temperature T , three gases enclosed in the volume V exert partial pressures p_1, p_2 , and p_3 , respectively.

Then

$$p_1 = \frac{n_1 RT}{V} \quad (\text{i})$$

$$p_2 = \frac{n_2 RT}{V} \quad (\text{ii})$$

$$p_3 = \frac{n_3 RT}{V} \quad (\text{iii})$$

where n_1 , n_2 , and n_3 are numbers of moles of the gases. Thus, the expression for total pressure will be

$$\begin{aligned} P_{\text{total}} &= p_1 + p_2 + p_3 \\ &= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V} \\ &= (n_1 + n_2 + n_3) \frac{RT}{V} \end{aligned} \quad (\text{iv})$$

On dividing p_1 by P_{total} , we get

$$\begin{aligned} \frac{p_1}{P_{\text{total}}} &= \left(\frac{n_1}{n_1 + n_2 + n_3} \right) \frac{RTV}{RTV} \\ &= \frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{n} = \chi_1 \end{aligned}$$

where $n = n_1 + n_2 + n_3$ and

χ_1 is called the mole fraction of the first gas.

$$\text{Thus, } p_1 = \chi_1 P_{\text{total}}$$

Similarly, for the other two gases we can write

$$p_2 = \chi_2 P_{\text{total}} \text{ and } p_3 = \chi_3 P_{\text{total}}$$

Thus a general equation can be written as

$$p_i = \chi_i P_{\text{total}} \quad (\text{v})$$

where p_i and χ_i are the partial pressure and mole fraction of the gas, respectively. Thus the partial pressure of a gas in a mixture is equal to the product of its mole fraction and the total pressure of the mixture. If the total pressure of the mixture of gases is known, Eq. (v) can be used to find out the pressure exerted by individual gases.

ILLUSTRATION 5.47

A neon dioxygen mixture contains 70.6 g O_2 and 167.5 g Ne. If pressure of the mixture of gases in the cylinder is 25 bar. what is the partial pressure of O_2 and Ne in the mixture?

$$\text{Sol. Moles of } \text{O}_2 (n_{\text{O}_2}) = \frac{70.6 \text{ g}}{32 \text{ g mol}^{-1}}$$

$$= 2.21 \text{ mol}$$

$$\text{Moles of Ne } (n_{\text{Ne}}) = \frac{167.5 \text{ g}}{20 \text{ g mol}^{-1}}$$

$$= 8.375 \text{ mol}$$

$$\text{Mole fraction of } \text{O}_2 (\chi_{\text{O}_2}) = \frac{2.21}{2.21 + 8.375}$$

$$= 0.21$$

$$\text{Mole fraction of Ne } (\chi_{\text{Ne}})$$

$$= 1 - 0.21 = 0.79$$

$$p_{\text{O}_2} = \chi_{\text{O}_2} \times P_{\text{total}}$$

$$= 0.21 \times (25 \text{ bar}) = 5.25 = \text{bar}$$

$$p_{\text{Ne}} = \chi_{\text{Ne}} \times P_{\text{total}}$$

$$= 0.79 \times (25 \text{ bar}) = 19.75 \text{ bar}$$

ILLUSTRATION 5.48

A certain quantity of gas occupies a volume of 0.8 L collected over water at 300 K and a pressure 0.92 bar. The same gas occupies a volume of 0.08 L at STP in dry conditions. Calculate the aqueous tension at 300 K.

Sol. Let the aqueous tension at 300 K be P bar.

The pressure of dry gas at 300 K = $(0.92 - P)$ bar

Now, $P_1 = (0.92 - P)$ bar, $P_2 = 1$ bar

$V_1 = 0.8$ L, $V_2 = 0.08$ L

$T_1 = 300$ K, $T_2 = 273.15$ K

Using gas equation, we get

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } P_1 = \frac{P_2 V_2 T_1}{V_1 T_2}$$

Substituting the values, we get

$$0.92 - P = \frac{1 \times 0.08 \times 300}{0.8 \times 273.15} = 0.109$$

$$\text{or aqueous tension} = 0.92 - 0.109 = 0.811 \text{ bar}$$

ILLUSTRATION 5.49

At sea level, the composition of dry air is approximately $\text{N}_2 = 75.5\%$, $\text{O}_2 = 23.2\%$, and Ar = 1.3% by mass. If the total pressure at sea level is 1 bar, what is the partial pressure of each component?

Sol. Let us consider 100 g of air.

$$\text{Moles of } \text{N}_2 (n_{\text{N}_2}) = \frac{W}{\text{Molar mass}} = \frac{75.5}{28} = 2.7$$

$$\text{Moles of } \text{O}_2 (n_{\text{O}_2}) = \frac{23.2}{32} = 0.725$$

$$\text{Moles of Ar } (n_{\text{Ar}}) = \frac{1.3}{40} = 0.0325$$

$$\text{Total moles} = 2.7 + 0.725 + 0.0325 = 3.4575$$

$$\text{Mole fraction of } \text{N}_2 (\chi_{\text{N}_2}) = \frac{2.7}{3.4575} = 0.781$$

$$\text{Mole fraction of } \text{O}_2 (\chi_{\text{O}_2}) = \frac{0.725}{3.4575} = 0.209$$

$$\text{Mole fraction of Ar } (\chi_{\text{Ar}}) = \frac{0.0325}{3.4575} = 9.39 \times 10^{-3}$$

$$p_{\text{N}_2} = P_{\text{total}} \times \chi_{\text{N}_2} = 1 \times 0.781 = 0.781 \text{ bar}$$

$$p_{\text{O}_2} = P_{\text{total}} \times \chi_{\text{O}_2} = 1 \times 0.209 = 0.209 \text{ bar}$$

$$p_{\text{Ar}} = P_{\text{total}} \times \chi_{\text{Ar}} = 1 \times 9.39 \times 10^{-3} = 9.39 \times 10^{-3} \text{ bar}$$

ILLUSTRATION 5.50

A 2 L flask contains 1.6 g of methane and 0.5 g of hydrogen at 27°C . Calculate the partial pressure of each gas in the mixture and hence calculate the total pressure.

Sol. Moles of $\text{CH}_4 = \frac{W}{\text{Molar weight}} = \frac{1.6}{16} \text{ mol} = 0.1 \text{ mol}$

Partial pressure of CH_4

$$p_{\text{CH}_4} = n_{\text{CH}_4} \times \frac{RT}{V} = \frac{0.1 \times 0.0821 \times 300}{2} = 1.23 \text{ atm}$$

Moles of $\text{H}_2 = \frac{W}{\text{Molar weight}} = \frac{0.5}{2} \text{ mol} = 0.25 \text{ mol}$

Partial pressure of H_2

$$p_{\text{H}_2} = n_{\text{H}_2} \times \frac{RT}{V} = \frac{0.25 \times 0.0821 \times 300}{2} = 3.079 \text{ atm}$$

$$\therefore \text{Total pressure} = p_{\text{CH}_4} + p_{\text{H}_2} = 1.23 + 3.079 = 4.31 \text{ atm}$$

ILLUSTRATION 5.51

20 g of hydrogen and 128 g of oxygen are contained in a 20 L flask at 200°C . Calculate the total pressure of the mixture. If a spark ignites the mixture, what will be the final pressure?

Sol. Moles of $\text{H}_2 = \frac{W}{\text{Molar weight}} = \frac{20}{2} = 10 \text{ mol}$

Moles of $\text{O}_2 = \frac{W}{\text{Molar weight}} = \frac{128}{32} = 4 \text{ mol}$

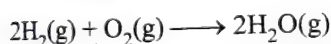
Total pressure

$$P = p_{\text{H}_2} + p_{\text{O}_2}$$

$$= (n_{\text{H}_2} + n_{\text{O}_2}) \frac{RT}{V}$$

$$= (10 + 4) \frac{(0.082 \times 473)}{20}$$

$$= 27.15 \text{ atm}$$



at the temperature of the spark.

Hence, 4 mol of oxygen will react with 8 mol of hydrogen to give 8 mol of water (g), and 2 mol of hydrogen will remain unreacted.

$$\text{Final pressure} = (n_{\text{H}_2} + n_{\text{O}_2}) \frac{RT}{V}$$

$$= \frac{(2 + 8) (0.082) \times 473}{20} = 19.39 \text{ atm}$$

ILLUSTRATION 5.52

The total pressure of a gaseous mixture of 2.8 g N_2 , 3.2 g O_2 , and 0.5 g H_2 is 4.5 atm. Calculate the partial pressure of each gas.

Sol. Number of moles = $\frac{\text{Mass}}{\text{Molar mass}}$

$$\text{Moles of } \text{N}_2 (n_{\text{N}_2}) = \frac{2.8}{28} = 0.1 \text{ mol}$$

$$\text{Moles of } \text{O}_2 (n_{\text{O}_2}) = \frac{3.2}{32} = 0.1 \text{ mol}$$

$$\text{Moles of } \text{H}_2 (n_{\text{H}_2}) = \frac{0.5}{2} = 0.25 \text{ mol}$$

$$\therefore \text{Total number of mole} = n_{\text{N}_2} + n_{\text{O}_2} + n_{\text{H}_2} = 0.1 + 0.1 + 0.25 = 0.45$$

Partial pressure a gas is

$$\frac{\text{Number of moles}}{\text{Total number of moles}} \times \text{Total pressure}$$

$$p_{\text{N}_2} = \frac{0.1}{0.45} \times 4.5 \text{ atm} = 1.0 \text{ atm}$$

$$p_{\text{O}_2} = \frac{0.1}{0.45} \times 4.5 \text{ atm} = 1.0 \text{ atm}$$

$$p_{\text{H}_2} = \frac{0.25}{0.45} \times 4.5 \text{ atm} = 2.5 \text{ atm}$$

ILLUSTRATION 5.53

I. Equal molecules of N_2 and O_2 are kept in a closed container at pressure P. If N_2 is removed from the system, then what will be the pressure of the container?

- a. P b. $2P$ c. $P/2$ d. P^2

II. Dalton's law of partial pressures is not applicable to

- a. Mixture of H_2 and N_2 b. Mixture of H_2 and Cl_2
c. Mixture of H_2 and CO_2 d. None

III. Equal volumes of all gases under the same conditions of temperature and pressure contain equal number of

- a. Atoms b. Molecules
c. Radicals d. Compound atoms

IV. 0.5 mol of H_2 , SO_2 , and CH_4 is kept in a container. A hole was made in the container. After 3 hours, the order of partial pressure in the container will be

- a. $p_{\text{SO}_2} > p_{\text{CH}_4} > p_{\text{H}_2}$ b. $p_{\text{H}_2} > p_{\text{SO}_2} > p_{\text{CH}_4}$
c. $p_{\text{CH}_4} > p_{\text{SO}_2} > p_{\text{H}_2}$ d. $p_{\text{CH}_4} > p_{\text{H}_2} > p_{\text{SO}_2}$

Sol.

I c. $P/2$ because $P_{\text{total}} = p_{\text{N}_2} + p_{\text{O}_2}$

II. b. The mixture of H_2 and Cl_2 because H_2 and Cl_2 react instantly to give HCl .

III. b. Molecules

IV. a. $p_{\text{SO}_2} > p_{\text{CH}_4} > p_{\text{H}_2}$

ILLUSTRATION 5.54

Why dry air is heavier than moist air?

Sol. Average molar weight of dry air is

$$= \frac{\% \text{ of } \text{N}_2 \times 28 + \% \text{ of } \text{O}_2 \times 32}{100}$$

Average molar weight of moist air is

$$= \frac{\% \text{ of } \text{N}_2 \times 28 + \% \text{ of } \text{O}_2 \times 32 + \% \text{ of } \text{H}_2\text{O} \times 18}{100}$$

Evidently, average molar weight of dry air is more and so is its density ($d = M/V$).

ILLUSTRATION 5.55

A vessel of 4.00 L capacity contains 4.00 g of methane and 1.00 g of hydrogen at 27°C . Calculate the partial pressure of each gas and also the total pressure in the container.

Sol. Let the partial pressure of hydrogen be p_{H_2} and the partial pressure of methane be p_{CH_4} .

The number of moles of hydrogen is

$$n_1 = \frac{1}{2} = 0.5 \text{ mol}$$

The number of moles of methane is

$$n_2 = \frac{4}{16} = 0.25 \text{ mol}$$

Now applying ideal gas equation for each gas, we get

$$p_{H_2} \times V = n_1 RT$$

$$p_{H_2} = \frac{n_1 RT}{V} = \frac{0.5 \times 0.0821 \times 300}{4} = 3.07 \text{ atm}$$

$$\text{Similarly, } p_{CH_4} V = n_2 RT$$

$$p_{CH_4} = \frac{n_2 RT}{V} = \frac{0.25 \times 0.0821 \times 300}{4} = 1.54 \text{ atm}$$

Total pressure of the gaseous mixture is

$$p_{H_2} + p_{CH_4} = 3.07 + 1.54 = 4.61 \text{ atm.}$$

5.9 DIFFUSION OF GASES

It is a matter of common observation that gases intermix freely without the help of any external agency. For example, if a cylinder containing hydrogen gas is inverted over another cylinder containing reddish-brown nitrogen dioxide gas and the lid separating the two cylinders is removed, then both the cylinders gradually become reddish brown. This indicates the intermixing of hydrogen and nitrogen dioxide forming a uniform mixture.

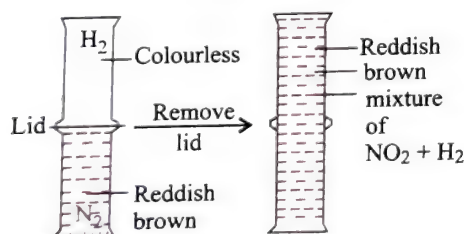


Fig. 5.19 Diffusion of gases

This property of intermixing of gases is referred to as diffusion. Diffusion may be defined as the process of intermixing of two or more gases irrespective of density relationship and without the help of external agency.

Diffusion in gases is attributed to the rapid movement of gas molecules and the existence of a large empty space between any two molecules. When the two gases are brought in contact with each other, the molecules of one gas move into the empty spaces of the other gas gradually, and this ultimately leads to the formation of a homogeneous mixture.

Effusion: Effusion is a process by which a gas under pressure escapes from the vessel through a small opening or orifice. Air escaping from a punctured tyre or football bladder and perfume molecules escaping through an atomizer are common examples of effusion. The process of effusion is always followed by diffusion.

5.9.1 GRAHAM'S LAW OF DIFFUSION/EFFUSION

Thomas Graham put forward a generalisation after studying the rates of diffusion of different gases, which is known after his name as Graham's law of diffusion. The law states:

Under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square roots of their densities.

The law can be mathematically put as $\left(r \propto \frac{1}{\sqrt{d}}\right)$, where r is

the rate of diffusion and d is the density of the gas.

Now, if there are two gases A and B having r_1 and r_2 as their rates of diffusions and d_1 and d_2 as densities, respectively, then

$$r_1 \propto \frac{1}{\sqrt{d_1}} \quad \text{and} \quad r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$\text{or } \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad (\text{at same } T \text{ and } p)$$

We know that molecular mass is twice the vapour density. Therefore, the above expression may be written as

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{\frac{Mw_2}{2}}{\frac{Mw_1}{2}}} = \sqrt{\frac{Mw_2}{Mw_1}}$$

where M_1 and M_2 are the molecular masses of the gases having densities d_1 and d_2 , respectively. Thus, Graham's law may also be stated as:

Under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square root of their molecular masses.

Again, the rate of diffusion of a gas is equal to the volume of the gas diffusing per unit time, i.e.,

$$\text{Rate of diffusion} = \frac{\text{Volume of the gas diffused}}{\text{Time taken for diffusion}}$$

$$\text{or } r = \frac{V}{t}$$

If V_1 and V_2 are the volumes of the gas diffusing in time t_1 and t_2 , respectively, then

$$r_1 = \frac{V_1}{t_1} \quad \text{and} \quad r_2 = \frac{V_2}{t_2}$$

Thus, putting the values of r_1 and r_2 , we arrive at the following formula:

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{Mw_2}{Mw_1}}$$

This implies that the time taken for the diffusion of equal volumes of two gases under similar conditions of temperature and pressure is directly proportional to the square root of their densities or molecular masses. Similarly, if $t_1 = t_2 = t$, then

$$\frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{Mw_2}{Mw_1}}$$

It means that the volumes of the two gases diffusing in the same time under similar conditions are inversely proportional to the square of their densities or molecular masses.

5.9.2 COMPARISON OF RATES OF DIFFUSION AT DIFFERENT TEMPERATURES OR PRESSURES

According to the Graham's law of diffusion, the rate of diffusion (r) of a gas at constant temperature is directly proportional to its

pressure as well as inversely proportional to the square root of its density or molecular weight.

$$r \propto \frac{1}{\sqrt{M}}$$

$$\text{or } r \propto \frac{P}{\sqrt{Mw}}$$

(at constant temperature)

$$\text{For gas I, } r_1 \propto \frac{P_1}{\sqrt{Mw_1}}$$

$$\text{For gas II, } r_2 \propto \frac{P_2}{\sqrt{Mw_2}}$$

$$\therefore \frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{Mw_2}{Mw_1}} \quad (\text{at constant } T)$$

Effect of temperature: If the rates of diffusion or effusion of two gases are compared at different temperatures but at constant pressures, then

$$\frac{r_1}{r_2} = \sqrt{\frac{T_1 d_2}{T_2 d_1}} = \sqrt{\frac{T_1 Mw_2}{T_2 Mw_1}}$$

T_1 and T_2 are the respective temperatures of the two gases.

Importance of Graham's law: Graham's law has a number of applications, some of which are as follows:

- It forms the basis for separating the isotopes of some elements.
- It provides a simple method for determining the densities and molecular masses of unknown gases by comparing their rates of diffusion or effusion with those of known gases.
- It is also useful in separating gases having different densities.

Atmolysis: The process of separation of two gases on the basis of their different rates of diffusion due to a difference in their densities is called atmolysis. It has been applied with success in separating isotopes and other gaseous mixtures.

ILLUSTRATION 5.56

Compare the rates of diffusion of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$

Sol. Let the rate of diffusion of $^{235}\text{UF}_6$ be r_1 and that of $^{238}\text{UF}_6$ be r_2 .

Now, the molecular mass of $^{235}\text{UF}_6$ is

$$M_1 = 235 + 6 \times 19 = 349$$

The molecular mass of $^{238}\text{UF}_6$ is

$$M_2 = 238 + 6 \times 19 = 352$$

According to Graham's law,

$$\frac{r_1}{r_2} = \sqrt{\frac{Mw_2}{Mw_1}} = \sqrt{\frac{352}{349}} = 1.004$$

Thus, $r(^{235}\text{UF}_6) : r(^{238}\text{UF}_6) = 1.004 : 1$.

ILLUSTRATION 5.57

The relative densities of oxygen and carbon dioxide are 16 and 22, respectively. If 25 cm^3 of carbon dioxide effuses out in 75s, what volume of oxygen will effuse out in 96s under similar conditions?

Sol. Here, volume of carbon dioxide

$$V_{\text{CO}_2} = 25 \text{ cm}^3$$

Time taken

$$t_{\text{CO}_2} = 75 \text{ s}$$

Let the volume of oxygen effused be

$$V_{\text{O}_2} = V \text{ cm}^3$$

Time taken

$$t_{\text{O}_2} = 96 \text{ s}$$

Relative density of carbon dioxide

$$d_{\text{CO}_2} = 22$$

Relative density of oxygen

$$d_{\text{O}_2} = 16$$

$$\text{Now, } \frac{r_{\text{O}_2}}{r_{\text{CO}_2}} = \sqrt{\frac{d_{\text{CO}_2}}{d_{\text{O}_2}}}$$

$$\text{or } \frac{\frac{V_{\text{O}_2}}{t_{\text{O}_2}}}{\frac{V_{\text{CO}_2}}{t_{\text{CO}_2}}} = \sqrt{\frac{22}{16}}$$

$$\text{or } \frac{V_{\text{O}_2}}{t_{\text{O}_2}} \times \frac{t_{\text{CO}_2}}{V_{\text{CO}_2}} = \sqrt{\frac{22}{16}}$$

Substituting the values, we get

$$\frac{V_{\text{O}_2} \times 75}{96 \times 25} = \sqrt{\frac{22}{16}} = 1.172$$

$$\text{or } V_{\text{O}_2} = \frac{1.172 \times 96 \times 25}{75} = 37.5 \text{ cm}^3$$

Thus, the volume of oxygen effused is 37.5 cm^3 .

ILLUSTRATION 5.58

A mixture of 50 mL of H_2 and 50 mL of O_2 is allowed to effuse through an effusimeter till the residual gas occupies 90 mL. What is the composition of (a) effused gas, (b) the residual gas?

Sol. According to Graham's law of diffusion,

$$\text{Rate of diffusion} = \sqrt{\frac{1}{\text{Molar weight}}}$$

$$\therefore \frac{\text{Rate of effusion of } \text{H}_2}{\text{Rate of effusion of } \text{O}_2} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{H}_2}}} = \sqrt{\frac{32}{2}} = 4$$

Volume of the mixture effused = $(50 + 50) - 90 = 10 \text{ mL}$

Let the volume of H_2 effused be $x \text{ mL}$.

Then the volume of O_2 effused will be $(10 - x) \text{ mL}$. So

$$\frac{x}{10 - x} = 4$$

$$\text{or } x = 4(10 - x) = 40 - 4x$$

$$\text{or } x = 8$$

Composition of the effused gas

 $H_2 = 8 \text{ mL}$ and $O_2 = 2 \text{ mL}$

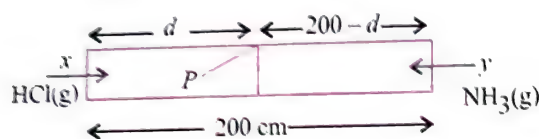
Composition of the residual gas

 $H_2 = 50 - 8 = 42 \text{ mL}$ and $O_2 = 50 - 2 = 48 \text{ mL}$ **ILLUSTRATION 5.59**

A straight glass tube has two inlets x and y at two ends. The length of the tube is 200 cm . HCl gas through inlet x and NH_3 gas through inlet y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance of P from x .

Sol. According to Graham's law of diffusion

$$\frac{\text{Rate of diffusion of } NH_3}{\text{Rate of diffusion of } HCl} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}} \quad (i)$$



$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{36.5}{17}} = \sqrt{2.147} = 1.465 : 1$$

$$d_{HCl} = \frac{1}{(1.465 + 1)} \times 200$$

$$= \frac{200}{2.465} = 81.13 \text{ cm}$$

$$d_{NH_3} = 200 - 81.13 = 118.87 \text{ cm}$$

ILLUSTRATION 5.60

One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, while 1 mol of an unknown fluoride of xenon at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formation of the compound.

Sol. We know that

$$r \propto \frac{P}{\sqrt{M}}$$

$$\text{Here, } r_{N_2} = \frac{1}{38} \text{ mol s}^{-1}$$

$$r_X = \frac{1}{57} \text{ mol s}^{-1}$$

(rate of diffusion of unknown fluoride of xenon)

For N_2

$$\frac{1}{38} = \frac{K \times 0.08}{\sqrt{28}} \quad (i)$$

For unknown gas,

$$\frac{1}{57} = \frac{K \times 1.16}{\sqrt{M_x}} \quad (ii)$$

Dividing (i) by (ii), we get

$$\frac{1}{38} \times \frac{1}{57} = \frac{0.8}{1.6} \times \left(\frac{M_x}{28}\right)^{1/2}$$

$$\therefore \frac{3}{2} = \frac{1}{2} \times \left(\frac{M_x}{28}\right)^{1/2}$$

$$\text{or } M_x = 252 \text{ g mol}^{-1}$$

Molar weight of xenon fluoride (XeF_x) is 252 .

$$131 + 19x = 252$$

(Xe = 131, F = 19)

$$\text{or } 19x = 252 - 131 = 121$$

$$\therefore x = \frac{121}{19} = 6.36$$

Hence, the xenon fluoride is XeF_6 .**ILLUSTRATION 5.61**

A balloon filled with ethylene is pricked with a needle and quickly dropped in a tank of H_2 gas under identical conditions. After a while, the balloon will

- a. Shrunk b. Enlarge
c. Completely collapse d. Remain unchanged in size

Sol.

$$\text{b. Rate of diffusion} \propto \sqrt{\frac{1}{M}}$$

Hence, H_2 will diffuse into balloon and its size will increase.

The correct choice is (b).

ILLUSTRATION 5.62

The volumes of ozone and chlorine diffusing in the same time are 35 mL and 29 mL , respectively. If the molecular weight of chlorine is 71 , calculate the molecular weight of ozone.

Sol. Applying Graham's law of diffusion, we get

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{Mw_2}{Mw_1}}$$

$$\text{or } \frac{V_1/t}{V_2/t} = \sqrt{\frac{Mw_2}{Mw_1}} \text{ or } \frac{V_1}{V_2} = \sqrt{\frac{Mw_2}{Mw_1}}$$

$$\text{or } \frac{V_{O_3}}{V_{Cl_2}} = \sqrt{\frac{M_{Cl_2}}{M_{O_3}}}$$

$$\text{or } \frac{35}{29} = \sqrt{\frac{71}{M_{O_3}}}$$

$$\text{or } M_{O_3} = 71 \times \left(\frac{29}{35}\right)^2 = 48.7$$

Hence, molecular weight of ozone is 48.7 g mol^{-1} .**ILLUSTRATION 5.63**

At 20°C , two balloons of equal volume and porosity are filled to a pressure of 2 atm , one with $14 \text{ kg } N_2$ and the other with 1 kg of H_2 . The N_2 balloon leaks to a pressure of $1/2 \text{ atm}$ in 1 hour . How long will it take for the H_2 balloon to reach a pressure of $1/2 \text{ atm}$?

Sol. We know that

$$\text{Rate of diffusion} \propto \sqrt{\frac{1}{\text{Density}}} \quad (i)$$

$$\therefore \text{Rate of diffusion of } N_2 (r_{N_2}) = \frac{\text{Pressure leaked}}{\text{Time}} = \frac{1/2 \text{ atm}}{10 \text{ h}}$$

$$\therefore \text{Rate of diffusion of } H_2 (r_{H_2}) = \frac{\text{Pressure leaked}}{\text{Time}} = \frac{1/2 \text{ atm}}{t}$$

Using Eq. (i), we get

$$\frac{r_{N_2}}{r_{H_2}} = \sqrt{\frac{d_{H_2}}{d_{N_2}}} \quad \text{or} \quad \frac{(1/2)/60}{(1/2)/t} = \sqrt{\frac{1}{14}}$$

$$\text{or } t = \sqrt{\frac{1}{14}} = 0.267 \text{ hour} = 0.267 \times 60 = 16.0 \text{ min}$$

ILLUSTRATION 5.64

Two balloons are filled with equal moles of hydrogen and helium. Which balloon will contract first if holes of same size are made in them?

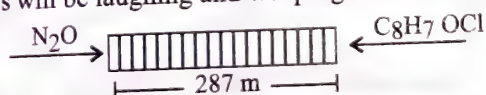
Sol. The balloon filled with hydrogen gas will contract first.

$$\frac{r_{H_2}}{r_{He}} = \sqrt{\frac{M_{He}}{M_{H_2}}}$$

Since the molecular mass of hydrogen is less, it will diffuse faster than helium.

ILLUSTRATION 5.65

A cinema hall has equidistant rows 1 m apart. The length of the cinema hall is 287 m and it has 287 rows. From one side of the cinema hall, laughing gas (N_2O) is released and from the other side, weeping gas ($C_6H_5COCH_2Cl$) is released. In which rows, spectators will be laughing and weeping simultaneously?



Sol. Molar weight of $C_6H_5COCH_2Cl = 8 \times 12 + 7 \times 1 + 16 + 35.5$
 $= 154.5 \text{ g}$

Molar weight of $N_2O = 2 \times 14 + 16 = 44 \text{ g}$

According to Graham's law of diffusion,

$$\frac{r_{N_2O}}{r_{C_6H_5COCH_2Cl}} = \sqrt{\frac{M_{C_6H_5COCH_2Cl}}{M_{N_2O}}} = \sqrt{\frac{154.5}{44}} = \sqrt{3.5} = 1.87 : 1$$

$$d_{N_2O} = \frac{1.87}{2.87} \times 287 = 187^{\text{th}} \text{ row from } N_2O \text{ side}$$

$$d_{C_6H_5COCH_2Cl} = \frac{1.0}{2.87} \times 287 = 100^{\text{th}} \text{ row from weeping gas side.}$$

Therefore, the spectator from the side of N_2O in the 187th row will be laughing and weeping simultaneously. Alternatively, the spectator from the side of weeping gas in the 100th row will be laughing and weeping simultaneously.

ILLUSTRATION 5.66

The relative rates of diffusion of ozone as compared to chlorine is 6:5. If the density of Cl_2 is 35.5, find out the density of ozone.

Sol. $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$
 $\frac{6}{5} = \sqrt{\frac{35.5}{d_1}}$
 $\therefore d_1 = 24.65$

ILLUSTRATION 5.67

127 mL of a certain gas diffuses in the same time as 100 mL of chlorine under the same conditions. Calculate the molecular weight of the gas.

Sol. $\frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{Mw_2}{Mw_1}}$
 $\frac{127}{100} = \sqrt{\frac{71}{Mw_1}}$
 $\therefore Mw_1 = 43.58$

ILLUSTRATION 5.68

50 volumes of hydrogen take 20 min to diffuse out of a vessel. How long will 40 volumes of oxygen take to diffuse out from the same vessel under the same conditions?

Sol. $\frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{d_2}{d_1}} = \frac{50/20}{50/t_2} = \sqrt{\frac{16}{1}}$
 $+ \frac{5 \times t_2}{2 \times 40} = 4$
 $\therefore t_2 = 64 \text{ min}$

ILLUSTRATION 5.69

Calculate the molecular weight of a gas X which diffuses four times as fast as another gas Y, which in turn diffuses twice as fast as another gas Z. Molecular weight of the gas Z is 128.

Sol. $r_y = 2r_z$
 $\frac{r_y}{r_z} = \frac{2r_z}{r_z} = \sqrt{\frac{128}{M_y}}$
 $4r_y = \frac{128}{4} = 32$
 $r_x = 4r_y$
 $\frac{r_x}{r_y} = \frac{4r_y}{r_y} = \sqrt{\frac{32}{M_x}}$
 $M_x = 2$

5.10 KINETIC MOLECULAR THEORY OF GASES

The various gas laws such as Boyle's law, Charles' law, etc, which we have studied so far, were based on experimental facts. There was no theoretical background for their justification. In order to explain the behaviour of gases and answer questions such as why

do they exert pressure or why a volume is inversely proportional to pressure, etc., it became necessary to develop a molecular theory to create a mental picture to provide explanation for our experimental observations. Maxwell Boltzmann, Clausius, etc., in 1857, suggested a theoretical model known as the *kinetic molecular theory of gases or microscopic model of gases*.

Microscopic model of gases: The assumptions of the kinetic theory are related to atoms and molecules which cannot be seen. Thus, the kinetic theory is said to give us a microscopic model of gases. The postulates of the theory are as follows:

- All gases are made up of a very large number of extremely small particles called *molecules*. All the molecules of a particular gas are identical in mass and size.
- The molecules are separated from one another by large spaces. Hence, the actual volume occupied by the molecules is negligible as compared to the total volume of the gas.
- The distances of separation between the molecules are so large that the forces of attraction or repulsion between them are negligible. They are completely independent of each other.
- The molecules of a gas are always in constant random motion. During their motion, they collide with one another and also against the walls of the container.
- The pressure exerted on the walls of the container is due to the bombardment of the molecules on the walls of the container.
- The collisions of the molecules with each other and with the walls of the container are perfectly elastic, i.e., there is no loss or gain of kinetic energy. However, there may be a redistribution of energy during such collisions.
- Since the molecules are moving with different velocities, they possess different kinetic energies. However, the average kinetic energy of the molecules of a gas is directly proportional to the absolute temperature of the gas.

Justification for the postulates: There is ample evidence in favour of the postulates of the kinetic theory as described below:

- The first postulate is in accordance with the particle nature of matter.
- The high compressibility of gases provides ample proof of the existence of large empty spaces between the gas molecules. The presence of large empty spaces will further become clear from the following example:

Assuming N_2 molecules to be spherical with radius (r) 2×10^{-8} cm, let us calculate the volume of a molecule and percentage of empty space in 1 mol of nitrogen at STP.

- Volume of the nitrogen molecule is

$$\frac{4}{3}\pi r^3 = \frac{4 \times 22 \times (2.00 \times 10^{-8} \text{ cm})^3}{3 \times 7}$$

$$= 3.35 \times 10^{-23} \text{ cm}^3 \text{ per molecule}$$

- Volume of 1 mol (6.02×10^{23}) of nitrogen molecules is $3.35 \times 10^{-23} \text{ cm}^3 \times 6.02 \times 10^{23} = 20.16 \text{ cm}^3$

Volume of 1 mol of nitrogen at STP is 22400 cm^3

Empty space = $(22,400 - 20.16) \text{ cm}^3 = 22379.84 \text{ cm}^3$

$$\% \text{ Empty space} = \frac{22379.84}{22400} \times 100 = 99.91\%$$

Thus, it is quite clear that an overwhelming amount of space in a gas is empty and the particles of the gas occupy only a tiny fraction of volume.

- The third postulate is supported by a simple observation that when pressure is released from a highly compressed gas, it expands indefinitely, and its tendency to occupy the whole space available implies that the movement of molecules occurs away from one another. This is possible if the attractive forces between the molecules are negligible.
- Dust particles or smoke particles are found to be in constant zigzag movement called Brownian movement. This is evident due to the fact that they are being tossed about by the fast moving molecules of the gas present in air.
- Since the molecules are continuously moving, they collide not only with one another but also with the walls of the container. Since a large number of molecules are hitting the walls, they exert a significant push or an outward force on the walls. The force exerted on a unit area of the wall is called pressure. This concept is supported by the inflation of a rubber balloon or a cycle tube when more and more air is pumped into it.
- The collisions of gas particles with one another and with the walls of the container are perfectly elastic. If it was not so, the force of friction would have slowed down the molecules after every collision. Ultimately, the gas would have come to rest and gradually settled down, but this does not happen. So the postulate must be correct.
- On increasing the temperature of the gas, molecular motion increases. In other words, individual velocities of molecules increase and hence the kinetic energy increases.

5.11 DIFFERENT TYPES OF MOLECULAR SPEEDS

Molecular speed is generally expressed in terms of

- Root mean square speed
- Average speed
- Most probable speed
- Root mean square speed (α or u_{rms}):** It is the square root of the mean of the squares of speeds of various molecules of the gas at a given temperature. If V_1, V_2, V_3, \dots are the speeds of different molecules, then the total KE of N molecules is the sum of the kinetic energies of individual molecules.

$$\text{Total KE} = \frac{1}{2}mV_1^2 + \frac{1}{2}mV_2^2 + \frac{1}{2}mV_3^2 + \dots$$

Let V be the velocity possessed by each of the molecules. Therefore,

$$\text{Total KE} = N \frac{1}{2}mV^2$$

$$\text{or } \frac{1}{2}m \times N \times V^2 = \frac{1}{2}mV_1^2 + \frac{1}{2}mV_2^2 + \frac{1}{2}mV_3^2 + \dots$$

$$\text{or } N \times V^2 = V_1^2 + V_2^2 + V_3^2 + \dots$$

$$V_{\text{rms}}^2 (\text{or } u_{\text{rms}}^2) = \frac{V_1^2 + V_2^2 + V_3^2 + \dots}{N}$$

$$\therefore u_{\text{rms}} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \dots}{N}}$$

Root mean square speed is given by the expressions

$$u_{\text{rms}} = \sqrt{\frac{3PV}{Mw}} = \sqrt{\frac{3RT}{Mw}} = \sqrt{\frac{3P}{d}}$$

d is the density of the gas.

- b. **Average speed:** It is the average of the speeds of different molecules of the gas at a particular temperature.

If V_1, V_2, V_3, \dots are the speeds of different molecules, then

$$\bar{v} \text{ (or } u_{\text{av}}) = \frac{V_1 + V_2 + V_3 + \dots}{N}$$

Average speed is given by the expression

$$\bar{v} \text{ (or } u_{\text{av}}) = \sqrt{\frac{8RT}{\pi Mw}}$$

$$\text{or } u_{\text{av}} = 0.9213 \times u_{\text{rms}}$$

$$\text{or } u_{\text{rms}} = 1.085 \times u_{\text{av}}$$

- c. **Most probable speed (α or u_{mp}):** It is the speed possessed by the maximum fraction of molecules of the gas at a particular temperature. It is given by the expression

$$\alpha \text{ (or } u_{\text{mp}}) = \sqrt{\frac{2RT}{Mw}} \text{ (Mw is the molecular mass of the gas)}$$

$$\text{or } u_{\text{mp}} = \left(\sqrt{\frac{2}{3}}\right) \times u_{\text{rms}} = 0.816 \times u_{\text{rms}}$$

$$\text{or } u_{\text{rms}} = 1.224 \times u_{\text{mp}}$$

Relationship between different types of speeds: The different types of speeds are related as shown below:

$$\alpha(\text{MPV}) : u(\text{AV}) : u(\text{RMS}) = 1 : 1.128 : 1.224$$

$$u(\text{RMS}) : u(\text{AV}) : \alpha(\text{MPV}) = 1 : 0.921 : 0.816$$

It is observed that the molecular velocity of any gas is proportional to the square root of the absolute temperature.

Average kinetic energy of gas molecules: The average kinetic energy of gas molecules can be calculated on the basis of the kinetic gas equation. According to kinetic gas equation.

$$P = \frac{1}{3} \left(\frac{N}{V} \right) m u^2$$

For 1 mol of the gas,

$$PV = \frac{1}{3} N_A m u^2 \quad [N = N_A \text{ for 1 mol}]$$

Also for 1 mol of an ideal gas, $PV = RT$

$$\therefore \frac{1}{3} N_A m u^2 = RT$$

$$\text{or } \frac{1}{2} \times \frac{2}{3} N_A m u^2 = RT \text{ or } \frac{1}{2} m u^2 = \frac{3}{2} RT$$

Now, $\frac{1}{2} m u^2$ represents the average kinetic energy (KE) of the molecule.

$$\therefore \text{KE} = \frac{3}{2} RT \text{ mol}^{-1} \text{ or } \text{KE} = \frac{3}{2} kT \text{ molecule}^{-1}$$

where $k = \frac{R}{N_A}$ (k is called the Boltzmann constant)

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ molecules}}$$

$$= 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$$

Since R or k are constants, it can be concluded that KE of gas is proportional to T .

5.11.1 EXPLANATION OF GAS LAWS BY THE KINETIC GAS EQUATION

The kinetic theory satisfactorily explains the gas laws as described below:

- a. **Boyle's law:** The kinetic molecular theory assumes that the pressure exerted by a gas is due to the bombardment of its molecules on the walls of the container. Thus, the pressure depends upon the number of molecular impacts or collisions per unit area of the walls per second.

If the temperature is kept constant, the average speed of the molecules $\left(\frac{1}{2} m v^2 \propto T\right)$ remains the same. Now

if the volume is increased, there will be less number of molecules colliding each unit area of the vessel in unit time. Consequently, the pressure will decrease. On the other hand, if volume is decreased, there will be more molecules in a given volume and, hence, pressure will increase. Thus, it can be concluded that at a given temperature, the pressure exerted by a gas is inversely proportional to the volume. This is *Boyle's law*.

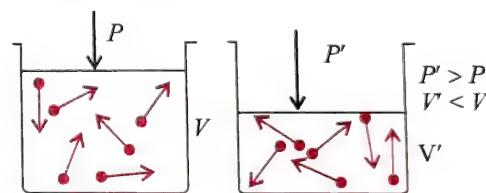


Fig. 5.20 Effect of decrease in volume

Deduction of Boyle's law from the kinetic gas equation:

According to the kinetic gas equation,

$$PV = \frac{1}{3} m n u^2 = \frac{2}{3} \times \frac{1}{2} m n u^2 = \frac{2}{3} \times \frac{1}{2} M u^2$$

(where $m \times n = M$ is the total mass of the gas)

But $\frac{1}{2} M u^2 = \text{kinetic energy of the gas}$

$$\therefore PV = \frac{2}{3} \text{KE} \quad (\text{i})$$

Further, according to one of the postulates of the kinetic theory of gases,

KE \propto Absolute temperature (T)

$$\text{or KE} = kT \quad (\text{ii})$$

where k is the constant of proportionality.

Putting this value in Eq. (i), we get

$$PV = \frac{2}{3} kT \quad (\text{iii})$$

Hence, at constant temperature, Eq. (iii) becomes

$PV = \text{constant}$, which is Boyle's law.

- b. **Charles' law:** When the temperature of a gas is increased, the kinetic energy of its molecules increases, $\left(\frac{1}{2} m v^2 \propto T\right)$. As a result, the velocity of the molecules

increases. Consequently, they collide with the walls of the container more frequently and more vigorously. Therefore, the pressure of the gas is expected to increase. However, if the pressure is to be kept constant, the force due to molecular collisions on the walls must be kept same. This is only possible if the volume of the gas increases, i.e., if the gas expands. On the other hand, if the temperature is decreased, the average velocity of the molecules decreases and, therefore, the pressure decreases. To keep the pressure constant, the volume of the gas must decrease so that the force due to collisions per unit area remains same.

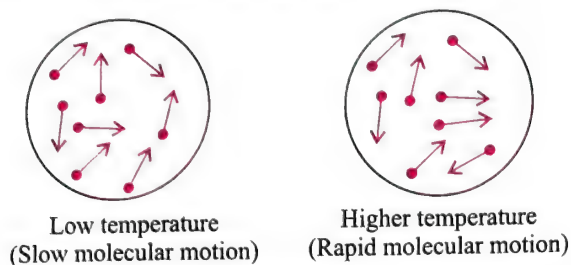


Fig. 5.21 Effect of increase in temperature

Thus, it can be concluded that at given pressure, the volume of the gas increases with a rise in temperature and decreases with a decrease in temperature. Hence, volume is directly proportional to temperature at constant pressure. This is *Charles' Law*.

Deduction from kinetic gas equation: Deducing Boyle's law from the kinetic gas equation, we have

$$PV = \frac{2}{3}kT \quad (i)$$

This may be rearranged as

$$\frac{V}{T} = \frac{2k}{3P} \quad (ii)$$

As in Eq. (ii), $2/3$ is constant, k is also constant; hence, if P is kept constant, $V/T = \text{constant}$.

This is *Charles' law*.

- c. **Dalton's law.** In the absence of attractive forces, the particles of a gas behave independent of one another. The same is true even if there are more than one type of molecules as in a mixture of non-reacting gases. Being independent, the number of molecules colliding per unit area of the walls per second, at a given temperature and for a fixed amount of the gas, is same. This implies that the partial pressure of the gas will be unaffected by the presence of the molecules of other gases. However, the total pressure exerted is due to the impact of the molecules of all the gases. Accordingly, the total pressure will be the sum of the partial pressures of the gases. This is *Dalton's law*.

Deduction from kinetic gas equation: Let us consider only two gases. According to the kinetic gas equation,

$$PV = \frac{1}{3}mnu^2$$

$$\text{or } P = \frac{1}{3} \frac{mnu^2}{V}$$

Now if only the first gas is enclosed in the same vessel (so that V is constant), then the pressure exerted will be

$$P_1 = \frac{1}{3} \frac{m_1 n_1 u_1^2}{V}$$

Again, if only the second gas is enclosed in the same vessel (at constant V), then the pressure exerted will be

$$P_2 = \frac{1}{3} \frac{m_2 n_2 u_2^2}{V}$$

Now let both the gases be enclosed in the same vessel. As the gases do not react with each other, the total pressure exerted will be

$$P = \frac{1}{3} \frac{m_1 n_1 u_1^2}{V} + \frac{1}{3} \frac{m_2 n_2 u_2^2}{V} = P_1 + P_2$$

Similarly, if more than two gases are present, then the total pressure is $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$

- d. **Graham's law of diffusion:** The rate of diffusion or effusion can be assumed to be directly proportional to the root mean square speed. Thus

$$\frac{r_1}{r_2} = \sqrt{\frac{u_1^2}{u_2^2}} \quad (i)$$

We know

$$u^2 = \frac{3PV}{Mw} \text{ or } \frac{3RT}{Mw} \quad (ii)$$

M is the molar mass of gas.

Using Eq. (ii) in Eq. (i), we get

$$\frac{r_1}{r_2} = \sqrt{\frac{3RT}{Mw_1}} \div \sqrt{\frac{3RT}{Mw_2}}$$

$$\text{Thus, } \frac{r_1}{r_2} = \sqrt{\frac{Mw_2}{Mw_1}}$$

This is *Graham's law of diffusion*.

ILLUSTRATION 5.70

Calculate the average kinetic energy of 8 g molecules of methane at 27°C in joule. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Sol. Total kinetic energy $= n \left(\frac{3}{2} RT \right)$

when n is the number of moles

$$\text{Moles of methane} = \frac{W}{\text{Molar weight}} = \frac{8}{16} = 0.5 \text{ mol}$$

$$\therefore \text{KE} = 0.5 \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ J}$$

Therefore, average kinetic energy is

$$= \frac{1870.65}{6.023 \times 10^{23} \times 0.5} = 6.21 \times 10^{-21} \text{ J}$$

ILLUSTRATION 5.71

The temperature at which the average speed of a gas molecule is double at 17°C is

- a. 34°C b. 68°C c. 162°C d. 887°C

Sol. d. $T_1 = 273 + 17 = 290 \text{ K}$, $T_2 = ?$

$$(u_{av})_1 \propto \sqrt{T_1} \quad (i)$$

$$(u_{av})_2 = 2(u_{av})_1 \propto \sqrt{T_2} \quad (ii)$$

Divide (ii) by (i)

$$\frac{2(u_{av})_1}{(u_{av})_1} = \sqrt{\frac{T_2}{T_1}}$$

$$\begin{aligned} T_2 &= 4T_1 = 4 \times 290 \text{ K} \\ &= 1160 \text{ K} \\ &= 1160 - 273 = 887^\circ\text{C} \end{aligned}$$

ILLUSTRATION 5.72

Calculate the u_{rms} of O_2 molecule at 27°C ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Sol. Using SI units:

$$\text{Mw of } O_2 = 32 \times 10^{-3} \text{ kg mol}^{-1}$$

$$\begin{aligned} u_{rms} &= \sqrt{\frac{3RT}{Mw}} \quad (T = 273 + 27 = 300 \text{ K}) \\ &= \sqrt{\frac{3 \times 8.314 \times 300}{32 \times 10^{-3}}} \\ &= \sqrt{233831.25} \\ &= 483.5 \text{ ms}^{-1} \end{aligned}$$

Using C.G.S. units:

$$R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mole}^{-1}$$

$$\text{Mw of } O_2 = 32 \text{ g mol}^{-1}$$

$$\begin{aligned} u_{rms} &= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}} \\ &= 4.835 \times 10^4 \text{ cm s}^{-1} \end{aligned}$$

ILLUSTRATION 5.73

The average velocity of CO_2 at the temperature $T_1 \text{ K}$ and maximum (most) probable velocity of CO_2 at the temperature $T_2 \text{ K}$ is $9 \times 10^4 \text{ cm s}^{-1}$. Calculate the values of T_1 and T_2 .

Sol. Given

$$\begin{aligned} \text{Average speed} &= \text{Most probable speed} \\ &= 9 \times 10^4 \text{ cm s}^{-1} \text{ or } 9 \times 10^2 \text{ m s}^{-1} \end{aligned}$$

We know,

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi M_w}} \quad (i)$$

$$\text{and most probable speed} = \sqrt{\frac{2RT}{M_w}} \quad (ii)$$

Equating equations (i) and (ii), we get

$$9 \times 10^2 = \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}}$$

$$\text{or } T_1 = 1682.5 \text{ K}$$

$$\text{and } 9 \times 10^2 = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}}$$

$$\text{or } T_2 = 2143.4 \text{ K}$$

ILLUSTRATION 5.74

The energy of an ideal gas is

- a. Completely kinetic
- b. Completely potential
- c. KE + PE
- d. All the above

Sol. a. Completely kinetic

ILLUSTRATION 5.75

At what temperature u_{rms} of a gas will become thrice of its value at STP?

Sol. $T_1 \text{ (STP)} = 273 \text{ K}$

$$T_2 = ?$$

$$\frac{3(u_{rms})_1}{(u_{rms})_1} = \sqrt{\frac{T_2}{T_1}}$$

$$\begin{aligned} \therefore T_2 &= 9 T_1 = 9 \times 273 \text{ K} \\ &= 2457 \text{ K} \end{aligned}$$

ILLUSTRATION 5.76

Calculate the temperature at which the average velocity of oxygen equals that of hydrogen at 20 K .

Sol. We know that

$$\text{Average velocity} = \left(\frac{3RT}{M_w} \right)^{1/2}$$

$$\text{i.e., average velocity} \propto \left(\frac{T}{M_w} \right)^{1/2}$$

Let c_{O_2} and c_{H_2} be the average velocities of O_2 and H_2 , respectively, then

$$\frac{v(O_2)}{v(H_2)} = \left[\frac{\frac{T_1}{M_{O_2}}}{\frac{T_2}{M_{H_2}}} \right]^{1/2} = 1$$

$$\text{or } \frac{T_1}{M_{O_2}} = \frac{T_2}{M_{H_2}}$$

$$\frac{T_1}{32 \text{ g mol}^{-1}} = \frac{T_2}{2 \text{ g mol}^{-1}}$$

$$\therefore T_1 = \left(\frac{32}{2} \right) T_2 = 16 \times 20 \text{ K} = 320 \text{ K}$$

ILLUSTRATION 5.77

Which of the following gases will have the highest RMS velocity at 25°C ?

- a. O_2
- b. CO_2
- c. SO_2
- d. CO

Sol.

d. CO gas, because root mean square velocity = $\left(\frac{3RT}{M_w}\right)^{1/2}$

$$\text{i.e., RMS} \propto \left(\frac{1}{M_w}\right)^{1/2}$$

CO has the lowest molecular mass; hence, it has the highest RMS velocity.

ILLUSTRATION 5.78

Which of the following expressions correctly represents the relationship between the average molar kinetic energies (KE) of CO and N₂ molecules at the same temperature?

- a. $\overline{\text{KE}}_{\text{CO}} = \overline{\text{KE}}_{\text{N}_2}$ b. $\overline{\text{KE}}_{\text{CO}} > \overline{\text{KE}}_{\text{N}_2}$
c. $\overline{\text{KE}}_{\text{CO}} < \overline{\text{KE}}_{\text{N}_2}$ d. All of the above

Sol.

a. $\overline{\text{KE}}_{\text{CO}} = \overline{\text{KE}}_{\text{N}_2}$, because

Average $\overline{\text{KE}} = \frac{3}{2}RT$. It does not depend upon the nature of the gas.

ILLUSTRATION 5.79

The ratio of the root mean square velocity of H₂ at 50 K to that of O₂ at 800 K is

- a. 4 b. 2 c. 1 d. $\frac{1}{4}$

Sol.

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M_w}}; \quad u_{\text{rms}} \propto \sqrt{\frac{T}{M_w}}$$

$$\therefore \frac{u_{\text{rms}}(\text{H}_2 \text{ at } 50 \text{ K})}{u_{\text{rms}}(\text{O}_2 \text{ at } 800 \text{ K})} = \sqrt{\frac{50}{2} \times \frac{32}{800}} = 1$$

So the correct choice is (c).

ILLUSTRATION 5.80

If for two gases of molecular weights M_A and M_B at temperatures T_A and T_B , $T_A M_B = T_B M_A$, then which of the following properties has the same magnitude for both the gases?

- a. Density b. Pressure
c. KE per mole d. u_{rms}

Sol.

a. Density of gas (ρ) = $\frac{PM}{RT}$

$$\text{Since } \frac{M_B}{T_B} = \frac{M_A}{T_A},$$

Therefore, at the same pressure $\rho_A = \rho_B$. But if pressure is different, then $\rho_A \neq \rho_B$.

- b. The pressure of the gases will be equal if their densities are equal, otherwise not [as in case (a)].

c. KE per mole = $\frac{3}{2}RT$

Hence, it will be different for the two gases.

d. $u_{\text{rms}} = \sqrt{\frac{3RT}{M_w}}$

$$\text{Since } \frac{T_A}{M_{wA}} = \frac{T_B}{M_{wB}}, \quad u_{\text{rms}} \text{ of } A = u_{\text{rms}} \text{ of } B$$

ILLUSTRATION 5.81

Arrange the following in order of increasing density:

Oxygen at 25°C, 1 atm; Oxygen at 0°C, 2 atm;
Oxygen at 273°C, 1 atm

Sol. $d \propto \frac{1}{V}$

$$\text{and } V = \frac{RT}{P}$$

V for O₂ at 25°C, 1 atm

$$= \frac{R \times 298}{1} = 298 R$$

V for O₂ at 0°C, 2 atm

$$= \frac{R \times 273}{2} = 136.5 R$$

V for O₂ at 273°C, 1 atm

$$= \frac{R \times 446}{2} = 446 R$$

Hence, the increasing order of density will be O₂ at 273°C, 1 atm; O₂ at 25°C, 1 atm; O₂ at 0°C, 2 atm.

ILLUSTRATION 5.82

- I. How is the pressure of a gas in a mixture related to the total pressure of the mixture?
- II. What would have happened to the pressure of a gas if the collisions of its molecules had not been elastic?

Sol.

- I. Partial pressure of the gas
= Mole fraction of the gas \times Total pressure
- II. Pressure would have ultimately become zero because molecular collisions would have slowed down to almost zero velocity.

ILLUSTRATION 5.83

Two bulbs A and B of equal capacity are filled with He and SO₂ respectively, at the same temperature.

- a. If the pressures in the two bulbs are same, what will be the ratio of the velocities of the molecules of the two gases?
- b. At what temperature will the velocity of SO₂ molecules become half of the velocity of He molecules at 27°C?

- c. How will the velocities be affected if the volume of B becomes four times that of A?
- d. How will the velocities be affected if half of the molecules of SO_2 are removed from B?

Sol. Let the velocities of He and SO_2 be u_1 and u_2 .

$$a. \quad u_1 = \sqrt{\frac{3RT}{M_{\text{He}}}}, \quad u_2 = \sqrt{\frac{3RT}{M_{\text{SO}_2}}}$$

$$\frac{u_1}{u_2} = \sqrt{\frac{M_{\text{SO}_2}}{M_{\text{He}}}} = \sqrt{\frac{64}{4}} = 4$$

- b. Let the velocity of He be u_1 .

$$\text{Velocity of } \text{SO}_2 = \frac{u_1}{2}$$

$$u_1 = \sqrt{\frac{3RT_1}{M_{\text{He}}}}, \quad \frac{u_1}{2} = \sqrt{\frac{3RT_2}{M_{\text{SO}_2}}}$$

$$\sqrt{\frac{3RT_1}{M_{\text{He}}}} = 2 \times \sqrt{\frac{3RT_2}{M_{\text{SO}_2}}}$$

$$\sqrt{\frac{T_1}{M_{\text{He}}}} = 2 \times \sqrt{\frac{T_2}{M_{\text{SO}_2}}}$$

$$\frac{T_1}{M_{\text{He}}} = 4 \times \frac{T_2}{M_{\text{SO}_2}}$$

$$T_2 = \frac{300 \times 64}{4 \times 4} = 1200 \text{ K}$$

$$\text{Temperature} = 1200 - 273 = 927^\circ\text{C}$$

- c. Velocity given by the relation $u = \sqrt{\frac{3PV}{Mw}}$. When volume increases by four times, pressure becomes $1/4$ and PV remains constant. So there will be no change in the velocities.
- d. Since velocities do not depend on the number of molecules, there will be no change in velocities.

ILLUSTRATION 5.84

Calculate the root mean square velocity of nitrogen at 27° and 70 cm pressure. The density of Hg is 13.6 g cm^{-3} .

Sol. Volume V_2 at 27°C and 70 cm pressure is given by

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}$$

$$\frac{70 \text{ cm} \times V_2}{300 \text{ K}} = \frac{70 \text{ cm} \times 0.0224 \text{ cm}^3}{273 \text{ K}}$$

$$\therefore V_2 = 0.026725 \text{ cm}^3$$

$$\text{Pressure } P = \left(\frac{70}{76}\right) \times 1.01325 \times 10^5 \text{ N m}^{-2}$$

$$= 9.332 \times 10^4 \text{ N m}^{-2}$$

$$\therefore u_{\text{rms}} = \left(\frac{3PV}{M}\right)^{1/2}$$

$$= \left(\frac{3 \times 9.332 \times 10^4 \text{ N m}^{-2} \times 0.026725 \text{ m}^3 \text{ mol}^{-1}}{28 \times 10^{-3} \text{ kg mol}^{-1}}\right)^{1/2}$$

$$= 517 \text{ m s}^{-1}$$

ILLUSTRATION 5.85

Calculate the RMS velocity of chlorine molecules at 17°C and 800 mm pressure.

Sol. We know,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Here $P_1 = 760 \text{ mm Hg}$, $P_2 = 800 \text{ mm Hg}$

$V_1 = 22,400 \text{ mL}$, $V_2 = ?$

$T_1 = 273 \text{ K}$, $T_2 = 290 \text{ K}$

$$\therefore V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{760 \times 22,400}{273} \times \frac{290}{800} = 22600 \text{ mL}$$

$$u_{\text{rms}} = \left(\frac{3PV}{M}\right)^{1/2}$$

Here, $P = 800 \text{ mm} = 80 \text{ cm}$

$$= 80 \times 13.6 \times 981 \text{ dyn cm}^{-2}$$

$V = 22,600 \text{ mL}$

$M = 71 \text{ g mol}^{-1}$

$$\therefore u_{\text{rms}} = \left(\frac{3 \times 80 \times 13.6 \times 981 \times 22,600}{71}\right)^{1/2}$$

$$= \sqrt{0.1018} \times 10^5 \text{ cm s}^{-1}$$

ILLUSTRATION 5.86

- I. Two flasks A and B have equal volume. A is maintained at 300 K and B at 600 K . While A contains H_2 gas, B has an equal mass of CH_4 gas. Assuming ideal behaviour for both the gases, which of the following statement is true about the velocities of molecules?
- The molecules in flasks A and B are moving with the same velocity.
 - The molecules in flask A are moving two times faster than the molecules in flask B.
 - The molecules in flask B are moving two times faster than the molecules in flask A.
 - The molecules in flask A are moving four times faster than the molecules in flask B.
- II. Two flasks A and B of equal volume are at temperatures 100 K and 200 K containing H_2 and CH_4 , respectively. Which of the following is true about KE per mole (KE = kinetic energy).
- KE per mole of H_2 is twice that of CH_4 .
 - KE per mole of CH_4 is twice that of H_2 .

- c. KE per mole of H_2 is equal to that of CH_4 .
 d. KE per mole of CH_4 is thrice that of H_2 .
- III. Two flasks A and B of equal volume containing equal masses of H_2 and CH_4 gases are at 100 K and 200 K temperature, respectively. Which of the following is true about the total KE (kinetic energy)?
- Total KE of H_2 is four times that of CH_4 .
 - Total KE of CH_4 is four times that of H_2 .
 - Total KE of H_2 is two times that of CH_4 .
 - Total KE of CH_4 is two times that of H_2 .
- IV. The kinetic energy of molecules at constant temperature in gaseous state is
- More than those in the liquid state
 - Less than those in the liquid state
 - Equal to those in the liquid state
 - None of these

Sol.

I. b. KE per mole = $\frac{3}{2}RT$

$$\therefore KE \propto T$$

$$\frac{KE_1}{KE_2} = \frac{T_A}{T_B} = \frac{100}{200} = \frac{1}{2}$$

II. b. $\bar{\mu}_A = \sqrt{\frac{8RT_A}{\pi M_A}}$

$$\bar{\mu}_B = \sqrt{\frac{8RT_B}{\pi M_B}}$$

$$\frac{\bar{\mu}_A}{\bar{\mu}_B} = \sqrt{\frac{300}{2} \times \frac{16}{600}} = 2$$

$$\bar{\mu}_A = 2\bar{\mu}_B$$

III. a. Total KE = $K\bar{E}$ (per mole) \times Number of molecules

$$\text{Total KE}_A = \frac{3}{2}KT_A N_A$$

$$n_A = \frac{m}{2}, n_B = \frac{m}{16} \therefore \frac{n_A}{n_B} = 8$$

$$\therefore \frac{\text{Total KE}_A}{\text{Total KE}_B} = \frac{T_A N_A}{T_B N_B} = \frac{1}{2} \times 8 = 4$$

IV. c. As $KE = \frac{3}{2}RT$ in gaseous and liquid phase both.

5.12 MAXWELL'S DISTRIBUTION OF SPEEDS

It has already been pointed out that a gas is a collection of tiny particles separated from one another by large empty spaces and moving rapidly at random in all directions. In the course of their motion, they collide with one another and also with the walls of the

container. Due to frequent collisions, the speeds and directions of motion of the molecules keep on changing. Thus, all the molecules in a sample of gas do not have same speeds. Although it is not possible to find out the speeds of individual molecules, yet from probability considerations it has become possible to work out the distribution of molecules among different speeds. This distribution is referred to as the **Maxwell-Boltzmann** distribution in honour of the scientists who developed it. It may be noted that the distribution of speeds remains constant at a particular temperature although **individual speeds** of molecules may *change*. Maxwell plotted the fraction of molecules having different speeds against the speeds at a particular temperature. The curve so obtained is shown in Fig. 5.22 and is called Maxwell's distribution curve.

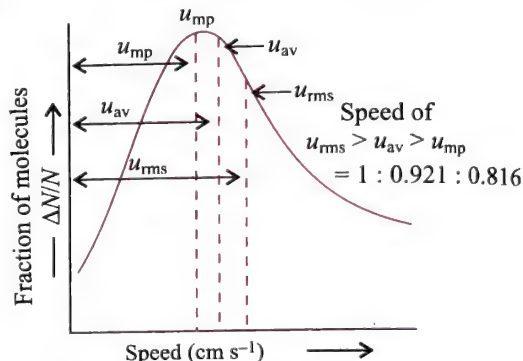


Fig. 5.22 Maxwell's distribution of speeds at a particular temperature

The important **features of Maxwell's distribution curve** can be summed up as follows:

- The fraction of molecules with very low or very high velocities (speeds) is very small.
- The fraction of molecules possessing higher and higher speeds goes on increasing till it reaches the peak, and thereafter it starts decreasing.
- The maximum fraction of molecules possesses a velocity (or speed) corresponding to the peak of the curve. The speed corresponding to the peak of the curve is referred to as the most probable speed.

The most probable speed may be defined as the speed possessed by the maximum fraction of molecules at a particular temperature.

Effect of temperature on distribution of speeds: It may be noted that the fraction of molecules having the most probable speed remains same so long as temperature remains same. However, on increasing the temperature of the gas, the molecular motion becomes rapid, and consequently the value of the most probable speed also increases. The entire distribution curve, in fact, shifts towards right with a rise in temperature as shown in Fig. 5.23. However, the area under the two curves remains same because it represents the number of molecules. The rise in temperature increases the fraction of molecules having higher speeds.

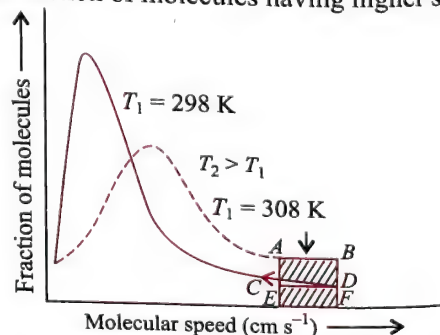


Fig. 5.23 Maxwell's distribution curves at different temperatures

5.13 BEHAVIOUR OF REAL GASES

5.13.1 DEVIATION FROM IDEAL GAS BEHAVIOUR

A gas that obeys the ideal gas laws and follows the ideal gas equation $PV = nRT$ under all conditions of temperature and pressure is called an 'ideal gas'. However, there is no gas that obeys the ideal gas equation under all conditions of temperature and pressure. Hence, the concept of ideal gas is only theoretical or hypothetical. Experiments show that at a low pressure and moderately high temperature, gases obey the laws of Boyle, Charles, and Avogadro approximately, but as the pressure is increased or the temperature is decreased, a marked departure from ideal behaviour is observed. Fig. 5.24 shows, for example, the type of deviation that occurs in Boyle's law for H_2 at room temperature.

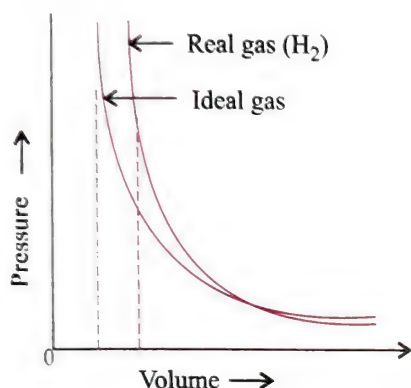


Fig. 5.24 Plot of pressure versus volume for real gas (H_2) and ideal gas

It is apparent that at a very high pressure, the measured volume of H_2 is more than the calculated volume. At low pressure, the measured and calculated volumes approach each other.

Deviation from ideal behaviour also becomes apparent when the PV vs P plot is drawn for several gases at 273 K.

At a constant temperature, PV will be constant (Boyle's law) and the PV vs P graph at all pressures will be a straight line parallel to the x-axis (Fig. 5.25).

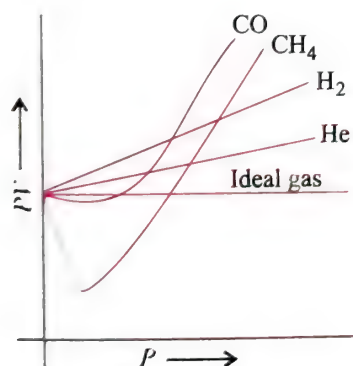


Fig. 5.25 Plot of PV vs P for real and ideal gases

It can be easily seen that at a constant temperature, the PV vs P plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen. In the curves for dihydrogen and helium, as the pressure increases, the value of PV also increases. The second type of plot is seen in other gases such as carbon monoxide and methane. In these plots, first there is a negative deviation from ideal behaviour. The PV value decreases with an increase in pressure and reaches

a minimum value characteristic of a gas. After that PV value starts increasing. The curve then crosses the line for an ideal gas and shows positive deviation continuously. It is thus found that real gases do not follow the ideal gas equation perfectly under all conditions.

The equation of state $PV = nRT$ derived from postulates of Kinetic Theory of Gases is valid for an *ideal gas* only. Real gases obey this equation only approximately and that too under conditions of high temperature and low pressure. The lower the temperature and higher the pressure the greater are the deviations from ideal behaviour in general more easily liquefiable and more soluble gases in water (such as CO_2 , SO_2 , NH_3 , HCl etc.) show larger deviations.

5.13.2 MEASUREMENT OF THE DEVIATION

The extent to which a real gas deviates from ideal behaviour can be conveniently displayed by plotting the ratio of the observed molar volume V_m to the ideal molar volume $V_{m,ideal} (= nRT/P)$ as a function of pressure at a constant temperature. This ratio is called the compressibility factor (Z) and can be expressed as

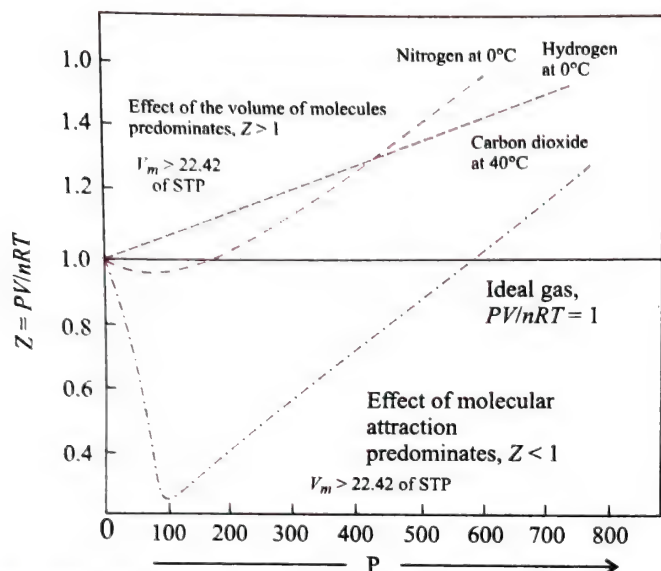
$$Z = \frac{V_m}{V_{m,ideal}} = \frac{PV_m}{nRT}$$

- In case of an ideal gas, $PV = nRT$. So $Z = 1$.
(under all condition of T and P)
- In case of a real gas, $PV \neq nRT$. So $Z \neq 1$.

Thus, in case of real gases, the value of Z can be less than 1 or greater than 1.

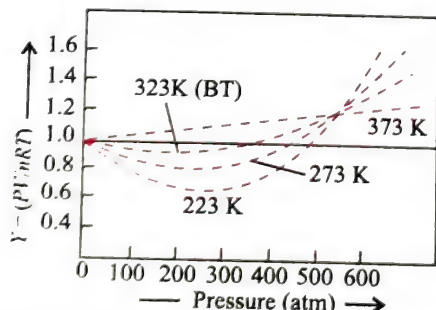
- Some observations from Z - P plots at 273 K
 - All gases have $Z = 1$, at low pressure i.e., they behave nearly ideally.
 - All gases have $Z > 1$ at high pressure i.e., $PV > PV_{ideal}$. Thus, all gases at high P are less compressible than an ideal gas.
 - At intermediate pressure and 273 K some gases (CO , CH_4 , NH_3 etc.) have $Z < 1$ i.e., $PV < PV_{ideal}$. Thus, these gases at 273 K and intermediate P are more compressible than an ideal gas.
 - Gases like H_2 , He at 273 K are seen to be less compressible than the ideal gas at all pressure i.e., $Z > 1$. However, if the temperature is sufficiently low (e.g., below 108 K for H_2 and below 33 K for He) these gases also give the same type of Z - P plots as shown by other gases at $0^\circ C$. On the other hand Z - P plots of gases like NH_3 , CO , CH_4 etc., are similar to those of H_2 , He at 273 K, if the temperature is sufficiently high.

The extent of deviation at any given temperature depends upon the nature of the gas. For example, CO_2 and N_2 are more compressible at low pressures and show negative deviation, but they are less compressible at high pressures and show positive deviation. Hydrogen gas, on the other hand, always shows positive deviation at $0^\circ C$. The behaviour of these gases has been described by the plot of Z against pressure in Fig. 5.26. The horizontal line in the figure refers to ideal behaviour.

Fig. 5.26 A plot of compressibility as a function of P for some gases at 0°C

d. Effect of temperature on deviation from ideal behaviour.

The Z - P plots of N_2 at different temperature varying from 200 K to 323 K (50°C) are shown in Fig. 5.27. It is seen that as temperature is raised, the dip in the curve becomes smaller and smaller. At 323 K, the curve seems to remain almost horizontal for an appreciable range of pressure (from 0 to 100 atm), showing thereby that $Z = 1$ under these conditions. In other words, the product PV remains constant and hence **Boyle's law** is obeyed within this range of pressure at 323 K. This temperature is called the **Boyle point** or **Boyle temperature**. Below this temperature, Z at first decreases, approaches a minimum and then increases as P is increased continuously. Above this temperature, Z shows a continuous rise with increase in P . The Boyle temperature is different for different gases.

Fig. 5.27 A plot of Z vs P for N_2 at different temperatures

5.13.3 CAUSES OF DEVIATIONS FROM IDEAL GAS BEHAVIOUR

The cause of the deviation from ideal behaviour may be attributed to the following two faulty assumptions of the kinetic theory of gases:

- There is no force of attraction between the molecules of a gas.
- The volume occupied by the molecules is negligible in comparison to the total volume of the gas.

Evidence for molecular attraction: If assumption (a) is correct, the gas will never liquefy. However, we know that gases do liquefy when cooled and compressed. The molecules of gases have weak van der Waals forces of attraction. This is also supported by the fact that when a compressed gas is passed through a porous plug of silk or cotton in adiabatic conditions, the emerging gas is found to be cooler than the entering gas (Joule-Thomson effect). This is because on expansion some work has to be done against the internal forces of attraction, which requires energy. This energy comes from the system itself.

Evidence for molecular volume: The molecules of a gas, however, do occupy a certain volume as can be seen from the fact that gases can be liquefied and solidified at a low temperature and high pressure. In the solid state, however, there is a considerable resistance to any further attempt at compression. It is, therefore, apparent that the molecules of a gas must have an appreciable volume, which is probably of the same order as that occupied by the same number of molecules in the solid state.

van der Waals equation: The general gas equation $PV = nRT$ is applicable to ideal gases only. van der Waals in 1873 modified the gas equation by introducing two correction terms, one for the volume and the other for the pressure, to make the equation applicable to real gases as well.

- Volume correction:** As pointed out earlier, the volume of the molecules of a gas is not negligible as compared to the total volume of the gas. This implies that the molecules are not free to move about in the entire volume (V) we observe. Thus, the free volume available to the gas molecules is smaller than the observed volume. In other words, the ideal volume (V_i) is smaller than the observed volume (V). Hence, a correction term has to be subtracted from the observed volume to get the ideal volume.

If b represents the effective volume occupied by the molecules of 1 mol of a gas, then for the amount n of the gas, V_i is given by

$$V_i = V - nb$$

where b is called the **excluded volume** or **co-volume**. The numerical value of b is four times the actual volume occupied by the gas molecules.

Excluded volume: If we consider only bimolecular collisions, then the volume occupied by a sphere of radius $2r$ represents the excluded volume per pair of molecules as shown in Fig. 5.28.

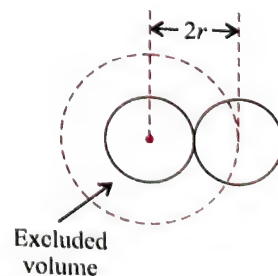


Fig. 5.28 Excluded volume per pair of molecule

Thus, the excluded volume per pair of molecules is

$$\frac{4}{3} \pi (2r)^3 = 8 \left(\frac{4}{3} \pi r^3 \right)$$

Excluded volume per molecule is

$$\frac{1}{2} \left[8 \left(\frac{4}{3} \pi r^3 \right) \right] = 4 \left[\frac{4}{3} \pi r^3 \right]$$

$= 4 \times \text{Volume occupied by a molecule}$

Since b represents excluded volume per mole of the gas, it is obvious that

$$b = N_A \left[4 \left(\frac{4}{3} \pi r^3 \right) \right]$$

where N_A is Avogadro number, and b is a constant depending on the nature of real gas.

Its unit is L mol^{-1} , which can be derived as follows:

$$V = nb$$

$$\text{or } b = \frac{V}{n} = \text{L mol}^{-1}$$

- b. Correction for force of attraction:** The pressure of a gas is due to the force with which its molecules collide with the walls of the container. Since intermolecular attractions cannot be neglected at low temperatures and high pressures, the molecules that strike the walls experience some backward drag due to the inward pull of adjacent molecules as shown Fig. 5.29. As a result, the molecules strike the walls with a smaller force because of the inward pull. Consequently, the pressure (P) that we observe is relatively smaller than the pressure if there were no attractive forces. In other words, the observed pressure (P) is smaller than the ideal pressure (P_i). Thus, in order to get the ideal pressure (P_i), a correction term has to be added to the observed pressure (P).

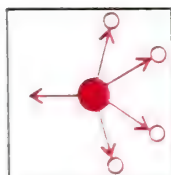


Fig 5.29. Molecule striking the walls experiences inward pull

Let the correction term be p . So

$$\text{Ideal pressure } P_i = P + p$$

Now, p is directly proportional to the square of the density or square of n/V . Thus,

$$p \propto (n/V)^2 = an^2/V^2$$

where a is the constant of proportionality called another van der Waals constant. Hence, ideal pressure

$$P_i = P + \frac{an^2}{V^2}$$

Here, n is the number of moles of the real gas, V is the volume of the gas, and a is a constant whose value depends upon the nature of the gas.

The value of a gives the idea of the magnitude of attractive forces between the molecules of the gas. Its units are $\text{atm L}^2 \text{mol}^{-2}$ or $\text{bar L}^2 \text{mol}^{-2}$, which can be derived as follows:

$$P = \frac{an^2}{V^2}$$

$$\therefore a = \frac{P \times V^2}{n^2} = \text{atm L}^2 \text{mol}^{-2}$$

The larger the value of a , the larger the intermolecular attraction of the gas molecules.

Substituting the values of ideal volume and ideal pressure, the modified equation is obtained as

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

where a and b are van der Waals constants. This equation is applicable to real gases and is known as the van der Waals equation. In Table 5.7, the values of van der Waals constants a and b are shown for different gases.

Table 5.7 van der Waals constants

Gas	a ($\text{kPa dm}^6 \text{mol}^{-2}$)	b ($\text{dm}^3 \text{mol}^{-1}$)
H ₂	21.764	0.02661
He	3.457	0.02370
N ₂	140.842	0.03913
O ₂	137.802	0.03183
Cl ₂	657.903	0.05622
NO	135.776	0.02789
NO ₂	535.401	0.04424
H ₂ O	553.639	0.03049
CH ₄	228.285	0.04278
C ₃ H ₈	877.880	0.08445
CO	150.468	0.03985
CO ₂	363.959	0.04267

5.13.4 EXPLANATION OF THE BEHAVIOUR OF REAL GASES BY VAN DER WAALS EQUATION

- a. At very low pressures,** V is very large. Hence, the correction term a/V^2 is so small that it can be neglected. Similarly, the correction term b can also be neglected in comparison to V . Thus, the van der Waals equation reduces to the form $PV = RT$. This explains why at very low pressures real gases behave like ideal gases.
- b. At moderate pressures,** V decreases. Hence, a/V^2 increases and cannot be neglected. However, V is still large enough in comparison to b so that b can be neglected. Thus, van der Waals equation becomes

$$\left(P + \frac{a}{V^2} \right) V = RT$$

$$\text{or } PV + \frac{a}{V} = RT$$

$$\text{or } PV = RT - \frac{a}{V}$$

$$\text{or } \frac{PV}{RT} = 1 - \frac{a}{RTV}$$

$$\text{or } Z = 1 - \frac{a}{RTV}$$

Thus, the compressibility factor is less than 1. As pressure is increased at constant temperature, V decreases so that the factor a/RTV increases. This explains why a dip in the plot of Z versus P is observed initially.

- c. At high pressures,** V is so small that b cannot be neglected in comparison to V . The factor a/V^2 is no doubt large, but

as P is very high, a/V^2 can be neglected in comparison to P . Thus, the van der Waals equation reduces to

$$P(V - b) = RT \text{ or } PV = RT + Pb$$

$$\text{or } \frac{PV}{RT} = 1 + \frac{Pb}{RT} \text{ or } Z = 1 + \frac{Pb}{RT}$$

Thus, the compressibility factor is greater than 1. As P is increased (at constant T), the factor Pb/RT increases. This explains why after minima in the curves, the compressibility factor increases continuously with pressure.

- d. **At high temperatures**, V is very large (at a given pressure) so that both the correction factors (a/V^2 and b) become negligible as in case (a). Hence, at a high temperature, real gases behave like ideal gases.

Explanation of the exceptional behaviour of hydrogen and helium: From Fig. 5.26, it may be seen that for H_2 and He, the compressibility factor Z is always greater than 1 and increases with an increase in pressure. This is because H_2 and He have very small molecules, which makes the intermolecular forces of attraction in them negligible. As a is very small, a/V^2 is negligible. The van der Waals equation, therefore, becomes

$$P(V - b) = RT$$

$$\text{or } PV = RT + Pb$$

$$\text{or } \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

Thus, PV/RT , i.e., Z , is greater than 1 and increases with an increase in the value of P at constant T .

Significance of van der Waals Constants

- Easily liquefiable gases such as SO_2 , NH_3 , H_2S and CO_2 have high values of a than permanent gases such as N_2 , O_2 , H_2 , and He. Furthermore, the value of a increases with the ease of liquefaction of the gas. Now since an easily liquefiable gas has greater intermolecular forces of attraction, the value of a is said to be a measure of the intermolecular forces of attraction.
- As b is the effective volume of the gas molecules, the constant value of b for any gas over a wide range of temperature and pressure indicates that the gas molecules are incompressible.

Limitations of the van der Waals Equation

The van der Waals equation is much more accurate than the ideal gas equation. It has been found that appreciable deviations can be seen even in this equation at very high pressures or very low temperatures. The reason is that the values of the van der Waals constants a and b do not remain constant over entire ranges of temperature and pressure. Their values remain constant only over specific ranges of temperature and pressure; hence, the van der Waals equation is also valid over specific ranges of temperature and pressure only.

5.13.5 DIFFERENCES BETWEEN IDEAL AND REAL GASES

The main differences between ideal and real gases are given below.

Ideal Gas

- An ideal gas obeys all the gas laws at all temperatures and pressures.
- The volume of molecules is negligible as compared to the total volume of the gas.

- Attractive forces among the molecules do not exist.
- It obeys the equation of state $PV = nRT$.
- It is hypothetical.

Real Gas

- A real gas obeys gas laws only at very low pressures and high temperatures.
- The volume of molecules is not negligible.
- Attractive forces among the molecules do not exist particularly at high pressures and low temperatures.
- It satisfies the van der Waals equation

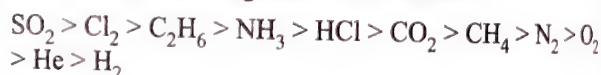
$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

- All existing gases are real.

Note:

- Real gases behave in nearly ideal manner at high temperature and low pressure.
- Easily liquefiable gases like CO_2 , SO_2 , HCl , NH_3 , etc., deviate more from ideal behaviour.
- At low pressures, the correction for intermolecular attraction ' a ' is more important than correction for molecular volume ' b '.
- The factor an^2/V^2 is called internal pressure of the gas and a is a measure of force of attraction between the molecules. Greater the value of a , greater is the ease of liquefaction of the gas.

Values of a for some gases are in the order



- The constant b is called co-volume or excluded volume.

$$b = 4 v_m N_A$$

where v_m the volume of a spherical molecule of radius r .

$$v = \frac{4}{3} \pi r^3$$

Values of b for some gases are in the order



- For any gas, at Boyle temperature $Z \approx 1$ for an appreciable range of pressure. Above Boyle temperature, Z continuously increases with increase in P and below, Boyle temperature, Z first decreases, approaches a minimum and then increases as P is increased continuously.

ILLUSTRATION 5.87

1 mol of SO_2 occupies a volume of 350 mL at 300 K and 50 atm pressure. Calculate the compressibility factor of the gas.

Sol. $P = 50 \text{ atm}$ $V = 350 \text{ mL} = 0.350 \text{ L}$

$n = 1 \text{ mol}$ $T = 300 \text{ K}$

We know that $Z = \frac{PV}{nRT}$.

$$Z = \frac{50 \text{ atm} \times 0.350 \text{ L}}{1 \text{ mol} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 0.711$$

Thus, SO_2 is more compressible than expected from ideal behaviour.

ILLUSTRATION 5.88

Calculate the pressure exerted by 8.5 g of ammonia (NH_3) contained in a 0.5 L vessel at 300 K. For ammonia, $a = 4.0 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 0.036 \text{ L mol}^{-1}$.

Sol. Number of moles of ammonia

$$n = \frac{8.5}{17} = 0.5 \text{ mol}$$

According to van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} = \frac{0.5 \times 0.082 \times 300}{(0.5 - 0.5 \times 0.036)} - \frac{4(0.5)^2}{(0.5)^2} = 21.51 \text{ atm}$$

ILLUSTRATION 5.89

2 mol of chlorine gas occupies a volume of 800 mL at 300 K and $5 \times 10^6 \text{ Pa}$ pressure. Calculate the compressibility factor of the gas. ($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$). Comment, whether the gas is more compressible or less compressible under these conditions.

Sol. Calculation of ideal volume (V_{ideal})

$$V_{\text{ideal}} = \frac{nRT}{P} = \frac{(2.0 \text{ mol})(0.083 \text{ bar K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(5 \times 10^6 / 10^5) \text{ bar}} = 1.004 \text{ L}$$

Now,

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{800 \text{ mL}}{1.004 \times 10^3 \text{ mL}} = 0.796$$

As Z is less than 1, it means that the gas is more compressible under these conditions.

ILLUSTRATION 5.90

Can we use Boyle's law to calculate the volume of a real gas from its initial state to final state during adiabatic expansion?

Sol. No, we cannot use Boyle's law to calculate volume during adiabatic expansion because temperature is lowered during adiabatic expansion, i.e., temperature does not remain constant, which violates Boyle's law.

ILLUSTRATION 5.91

The compressibility factor of gases is less than unity at STP. Therefore,

a. $V_m > 22.4 \text{ L}$

b. $V_m < 22.4 \text{ L}$

c. $V_m = 22.4 \text{ L}$

d. $V_m = 4.8 \text{ L}$

Sol. $Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$

If $Z < 1$, then $V_{\text{real}} < V_{\text{ideal}}$ (i.e., 22.4 L at STP)

Hence, the correct choice is (b).

ILLUSTRATION 5.92

The density of steam at 100°C and 10^5 Pa pressure is 0.6 kg m^{-3} . Calculate the compressibility factor of steam.

Sol. We know

$$Z = \frac{PV}{nRT} \quad \dots(i)$$

$$\text{and } d = \frac{PM}{RT} \quad \dots(ii)$$

Using (i) and (ii), we get

$$Z = \frac{PV}{(w/M)RT} = \frac{MPV}{wRT} = \frac{MP}{dRT}$$

Therefore, on substituting all the values, we get

$$Z = \frac{(18 \times 10^{-3} \text{ kg mol}^{-1}) \times 10^5 (\text{N m}^{-2})}{(0.6 \text{ kg m}^{-3}) \times (8.31 \text{ N m K}^{-1} \text{ mol}^{-1}) \times (373.15 \text{ K})} = 0.967$$

ILLUSTRATION 5.93

The compressibility factor ($Z = PV/nRT$) for N_2 at 223 K and 81.06 MPa is 1.95, and at 373 K and 20.265 MPa, it is 1.10. A certain mass of N_2 occupies a volume of 1.0 dm^3 at 223 K and 81.06 MPa. Calculate the volume occupied by the same quantity of N_2 at 373 K and 20.265 MPa.

Sol. For $T = 223 \text{ K}$, $P = 81.06 \text{ MPa}$, $Z = 1.95$, and $V = 1.0 \text{ dm}^3 = 10^3 \text{ cm}^3$, we have

$$n = \frac{PV}{ZRT} = \frac{81.06 \times 10^3}{1.95 \times 8.314 \times 223} = 22.42 \text{ mol}$$

Now, at $T = 373 \text{ K}$, $P = 20.265 \text{ MPa}$, $Z = 1.10$, the volume occupied will be

$$V = \frac{ZnRT}{P} = \frac{1.10 \times 22.42 \times 8.314 \times 373}{20.265} = 3774.0 \text{ cm}^3$$

$$\therefore V = 3.774 \text{ dm}^3$$

ILLUSTRATION 5.94

Calculate the pressure exerted by 22 g of CO_2 in 0.5 dm^3 at 300 K using (a) the ideal gas law and (b) the van der Waals equation. Given $a = 300.0 \text{ kPa dm}^6 \text{ mol}^{-2}$ and $b = 40.0 \text{ cm}^3 \text{ mol}^{-1}$.

Sol. Moles of $\text{CO}_2 = \frac{w}{\text{Molar weight}} = \frac{22 \text{ g}}{44 \text{ g mol}^{-1}} = 0.5 \text{ mol}$

$$V = 0.5 \text{ dm}^3, T = 300 \text{ K}, a = 300.0 \text{ kPa dm}^6 \text{ mol}^{-2}$$

$$b = 40.0 \text{ cm}^3 \text{ mol}^{-1} = 0.04 \text{ dm}^3 \text{ mol}^{-1}$$

a. From ideal gas law $P = \frac{nRT}{V}$, we have

$$P = \frac{(0.5)(8.314) \times 300}{0.5} = 2494.2 \text{ Pa} = 2.49 \times 10^3 \text{ kPa}$$

b. From the van der Waals equation, we get

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\therefore P = \frac{(0.5) \times (8.314) \times 300}{(0.5) - (0.5)(0.04)} - \frac{(0.5)^2 \times (300)}{(0.5)^2}$$

$$= 2598.12 \text{ kPa} - 300 \text{ kPa} = 2298.12 \text{ kPa}$$

ILLUSTRATION 5.95

Two van der Waals gases have the same value of b but different values of a . Which of these will occupy greater volume under identical conditions? If the gases have the same value of a but different values of b , which of them will be more compressible?

Sol. When two gases have the same value of b but different values of a , the gas having a larger value of a will occupy lesser volume. This is because the gas with a larger value of a will have larger forces of attraction and hence lesser distance between its molecules.

When two gases have the same value of a but different values of b , the smaller the value of b , the larger the compressibility because the gas with the smaller value of b will occupy lesser volume and hence will be more compressible.

ILLUSTRATION 5.96

What is the value of b (van der Waals constant) if the diameter of a molecule is 2.0 \AA ?

- a. $\approx 2.4 \text{ mL mol}^{-1}$ b. $\approx 4.8 \text{ mL mol}^{-1}$
c. $\approx 7.2 \text{ mL mol}^{-1}$ d. $\approx 9.6 \text{ mL mol}^{-1}$

Sol.

- d. $b = 4 \times \text{volume occupied by the molecules in 1 mol of a gas}$

$$= 4 \times \frac{4}{3} \times \pi r^3 \times N_A$$

$$= 4 \times \frac{4}{3} \times 3.1 \times (1 \times 10^{-8} \text{ cm})^3 \times 6 \times 10^{23}$$

$$= 96 \times 10^{-1} \approx 9.6 \text{ mL mol}^{-1}$$

Alternatively

Use Direct formula:

$$b \approx 96 \times 10^{23} \times r^3 = 96 \times 10^{23} \times (10^{-8})^3 \approx 9.6 \text{ mL mol}^{-1}$$

ILLUSTRATION 5.97

Calculate the molecular diameter of helium from its van der Waals constant b . ($b = 24 \text{ cm}^3 \text{ mol}^{-1}$)

Sol. Since $b = 4 \times \text{Volume occupied by the molecules in 1 mol of a gas}$

$$\text{or } b = 4 N_A \left(\frac{4}{3} \pi r^3 \right)$$

$$\therefore r = \left(\frac{3b}{16 N_A \pi} \right)^{1/3}$$

$$= \left\{ \frac{3 \times 24}{16 (6.023 \times 10^{23}) (3.14)} \right\}^{1/3}$$

$$= 1.335 \times 10^{-8} \text{ cm} = 133.5 \text{ pm}$$

$$\therefore d = 2r = 2 \times 133.5 \text{ pm} = 267 \text{ pm}$$

Alternatively

$$\text{Use direct formula}$$

$$b = 96 \times 10^{23} r^3$$

ILLUSTRATION 5.98

- I. The internal pressure loss of 1 mol of van der Waals gas over an ideal gas is equal to
 - a. Zero b. b^2 c. $\frac{a}{V^2}$ d. $b - \frac{a}{RT}$
- II. The van der Waals equation for CH_4 at low pressure is
 - a. $PV = RT - Pb$ b. $PV = RT - \frac{a}{V}$
 - c. $PV = RT + \frac{a}{V}$ d. $PV = RT + Pb$
- III. Which of the following can be most readily liquefied? The given value of a for NH_3 is 4.17, CO_2 is 3.59, SO_2 is 6.71, and Cl_2 is 6.49.
- IV. Out of NH_3 and N_2 , which will have
 - a. larger value of a b. larger value of b

Sol.

- I. $P + \frac{a}{V^2}$ is the pressure of the ideal gas, while P is the pressure of the real gas. Therefore, a/V^2 is the difference. Hence, the correct choice is (c).
- II. The van der Waals gas equation for 1 mol of gas is

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$
 At low P , volume is high. So $(V - b) \cdot V$

$$\therefore \left(P + \frac{a}{V^2} \right) V = RT$$
 or $PV = RT = \frac{a}{V}$
 Hence, the correct choice is (b).
- III. The van der Waals constant a shows the force of attraction between two molecules. Hence, the higher the value of a , the higher the attraction. Therefore, the gas will be readily liquefied. Therefore, SO_2 will be readily liquefied.
- IV. a. NH_3 will have a larger value of a because of H-bonding.
b. N_2 will have a larger value of b because of larger molecular size.

ILLUSTRATION 5.99

If volume occupied by CO_2 molecules is negligible, then calculate pressure $\left(\frac{P}{5.277} \right)$ exerted by one mole of CO_2 gas at 300 K. ($a = 3.592 \text{ atm L}^2 \text{ mol}^{-2}$)

Sol. $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

$$n = 1$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

If b is negligible

$$P = \frac{RT}{V} - \frac{a}{V^2}$$

The equation is quadratic in V thus

$$V = \frac{+RT \pm \sqrt{R^2T^2 - 4aP}}{2P}$$

Since V has one value at given P and T , thus numerical value of discriminant = 0

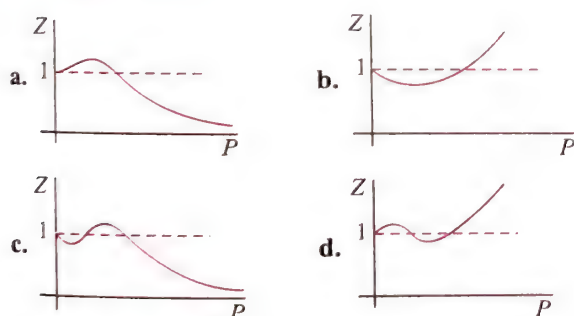
$$R^2T^2 = 4aP$$

$$P = \frac{R^2T^2}{4a} = \frac{(0.821)^2 (300)^2}{4 \times 3.592}$$

$$\therefore \frac{P}{5.277} = 8$$

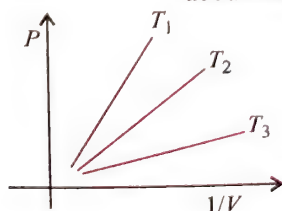
ILLUSTRATION 5.100

- I. According to the real gas equation, Z is equal to 1 for an ideal gas and Z is variable for a real gas. Suppose, in order to ease our calculations, we fixed $Z = 1$ for real gas and for ideal gas Z will become variable. Z vs P for an ideal gas will be similar to:



- II. The curve drawn below shows the variations of P as a function of $1/V$ for a fixed mass and temperature of an ideal gas. It follows from the curve that:

- a. $T_3 > T_2 > T_1$ b. $T_1 > T_2 > T_3$
c. $T_1 = T_2 = T_3$ d. Nothing can be predicted about temperatures



- III. If two gases have the same value of b but different values of a (a and b are van der Waals constants), which of the following statements is wrong?

- The gas having a larger value of a will occupy less volume.
- The gas having a larger value of a will occupy more volume.
- The gas having a larger value of a will have higher forces of attraction.
- The gas having a larger value of a will have lesser distance between the molecules.

- IV. If two gases have the same value of a but different values of b (a and b are van der Waals constants), which of the following statements is wrong?

- The gas having a smaller value of b has larger compressibility.
- The gas having a smaller value of b will occupy lesser volume.
- The gas having a smaller value of b has lesser compressibility.
- Both (a) and (b).

Sol.

- I. b.

- II. b. For ideal gas $PV = nRT$

$$\text{or } P = \frac{nRT}{V}$$

Therefore, the slope increases with temperature.

- III. b.

- IV. c.

ILLUSTRATION 5.101

- I. Which gas will liquefy easily (a and b are van der Waals constants)?
- Larger values of a and b
 - Smaller value of a but larger value of b
 - Smaller values of a and b
 - Larger value of a but smaller value of b
- II. The rise in compressibility factor (Z) with increasing pressure of a gas is due to
- van der Waals constant a
 - van der Waals constant b
 - Both (a) and (b)
 - Not related to either a or b
- III. At which of the following conditions can a gas be liquefied? T_c and P_c are critical temperature and pressure.
- $T = T_c$ and $P < P_c$
 - $T < T_c$ and $P = P_c$
 - $T > T_c$ and $P < P_c$
 - $T < T_c$ and $P < P_c$
- IV. Two equal-volume flasks A and B containing equal masses of H_2 and CH_4 are at 100 K and 200 K, respectively. Assuming ideal behaviour, which of the following statements about the compressibility factor (Z) is true?
- Z of $H_2 = Z$ of CH_4
 - Z of $H_2 = 4Z$ of CH_4
 - Z of $H_2 = 16Z$ of CH_4
 - Z of $H_2 = 2Z$ of CH_4

Sol.

I. d.

$$\text{II. b. } \left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Ignoring a/V^2 , since P is large

$$P(V - b) = RT$$

$$PV - Pb = RT$$

Dividing by RT , we get

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$Z - \frac{Pb}{RT} = 1$$

$$Z = 1 + \frac{Pb}{RT}$$

 Z increases as b increases, so it is independent of a .III. b. a. Incorrect since $P \geq P_c$ b. Correct since $P = P_c$ and $T < T_c$

IV. a. Both gases will have the same compressibility factor, i.e., 1, since both of them are ideal gases.

ILLUSTRATION 5.102

The van der Waals constants for a substance are $a = 300.003 \text{ kPa dm}^6 \text{ mol}^{-2}$ and $b = 40.8 \text{ cm}^3 \text{ mol}^{-1}$. Find the critical constants of this substance.

Sol. Given

$$a = 300.0 \text{ kPa dm}^6 \text{ mol}^{-2}$$

$$b = 40.0 \text{ cm}^3 \text{ mol}^{-1} = 40 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{i. } V_c = 3b = 3 \times 40.0 \text{ cm}^3 \text{ mol}^{-1} = 120.0 \text{ cm}^3$$

$$\begin{aligned} \text{ii. } P_c &= \frac{8a}{27b^2} \\ &= \frac{8 \times 300}{27 \times (40 \times 10^{-3})^2} = \frac{2400 \times 10^6}{43200} \\ &= 0.055 \times 10^6 \text{ kPa} \end{aligned}$$

$$\begin{aligned} \text{iii. } T_c &= \frac{8a}{27Rb} \\ &= \frac{8 \times 300}{27 \times 8.314 \times 40 \times 10^{-3}} = \frac{2400}{8979.12} \\ &= 0.2672 \times 10^3 = 267 \text{ K} \end{aligned}$$

$$\text{Hence, } V_c = 120.0 \text{ cm}^3, P_c = 0.055 \times 10^6 \text{ kPa, } T_c = 267 \text{ K}$$

ILLUSTRATION 5.103

I. The temperature below which a gas does not obey ideal gas laws is

- a. Critical temperature b. Inversion temperature
c. Boyle temperature d. Reduced temperature

II. An ideal gas obeying the kinetic theory of gases can be liquefied if

- a. Its temperature is more than its critical temperature (T_c)
b. Its pressure is more than its critical pressure (P_c)
c. Its pressure is more than P_c at a temperature less than T_c
d. It cannot be liquefied at any value of P and T

III. Which of the following relations is incorrect?

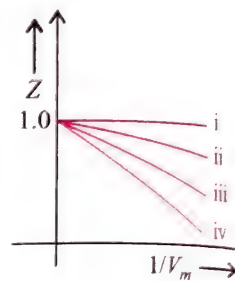
- a. $a = 3 P_c V_c^2$ b. $b = V_c/3$
c. $T_c = 8a/27 Rb$ d. $b = 3 V_c$

IV. The critical temperature of a substance is

- a. The temperature above which a substance can exist only as a gas
b. Boiling point of the substance
c. All are wrong.
d. Both (a) and (b)

V. Considering the graph, which of the following gases have the highest critical temperature T_c ?

- a. i b. ii
c. iii d. iv

**Sol.**

I. c. Boyle temperature

II. d. It cannot be liquefied at any value of P and T .

$$\text{III. b. } b = \frac{V_c}{3}$$

IV. b. The critical temperature of a substance is the temperature above which a substance can exist only as a gas.

V. d.

ILLUSTRATION 5.104

Gases possess characteristic critical temperature (T_c) which depends upon the magnitude of intermolecular forces between the gas particle. T_c of NH_3 and CO_2 are 405.5 K and 304.10 K respectively. Which of these gases will liquefy first when you start cooling from 500 K to their critical temperature?

Sol. NH_3 will liquefy first because its critical temperature will be reached first. Liquefaction of CO_2 will require more cooling.

5.14 OTHER EQUATIONS OF STATE FOR REAL GASES

Berthelot's equation: The Berthelot equation is given by

$$\left(P + \frac{n^2 a}{TV^2}\right)(V - nb) = nRT$$

where a and b are constants called Berthelot's constants (different from van der Waals constants), and these constants are characteristics of the gas.

Dieterici's equation: The Dieterici equation of state is given by

$$[P \exp(na/VRT)] [V - nb] = nRT$$

where a and b are constants and are characteristics of the gas.

Virial equation: The virial equation is an equation common to all three equations of state (van der Waals, Berthelot, Dieterici). All the three equations of state can be expressed approximately by the virial equation of state. The virial equation of state for 1 mol of a gas is

$$Z = \frac{PV_m}{RT} = 1 + B \frac{1}{V_m} + C \frac{1}{V_m^2} + D \frac{1}{V_m^3} + \dots$$

where B, C, D, \dots are temperature-dependent constants known as second, third, fourth, ... virial coefficients.

Boyle's temperature (T_b): It is the temperature at which a real gas exhibits almost ideal behaviour for a considerable range of pressure. Different gases have different values of T_b , which is related to the van der Waals constants a and b as follows:

$$T_b = a/Rb$$

Joule-Thomson effect: When a compressed gas is allowed to expand through a small orifice, cooling effect is caused and temperature falls. This is known as the Joule-Thomson effect. It was later observed that the Joule-Thomson effect is observed only if the gas goes below a certain temperature (which is different for different gases). This temperature is called **inversion temperature (T_i)**. It is related to the van der Waals constants as follows:

$$T_i = \frac{2a}{Rb}$$

- Cooling effect is caused only during expansion if the temperature of the gas is less than its T_i .
- If the temperature of the gas is greater than its T_i , then heating effect, i.e., negative Joule-Thomson effect is observed.
- Expansion of the gas at its T_i does not show cooling or heating effect, i.e., at T_i the Joule-Thomson effect is zero.

5.15 LIQUEFACTION OF GASES

According to the kinetic theory of gases, gases consist of tiny molecules widely separated from one another by large empty spaces (voids). The molecules are in a state of continuous rapid motion with negligible attractive forces between them. Every molecule has almost independent existence. This is particularly so when temperature is high and pressure is low. When the temperature of the gas is lowered, the volume of the gas and also the kinetic energy of the molecules decrease. The molecules become sluggish, and molecular motion becomes slow. The molecules come closer because they are unable to resist the attractive forces that start operating between them. As the process of decrease in temperature continues, the gas molecules go on moving closer and closer. Ultimately, at a sufficiently low temperature, the voids between the molecules become less than 10^{-5} cm and the gas changes into liquid. The effect of bringing the gas molecules closer and closer can also be achieved by increasing the pressure because this also causes a decrease in the volume of the gas. Thus, liquefaction of gas can be achieved by a decrease in temperature and by an increase in pressure as shown in Fig 5.30.

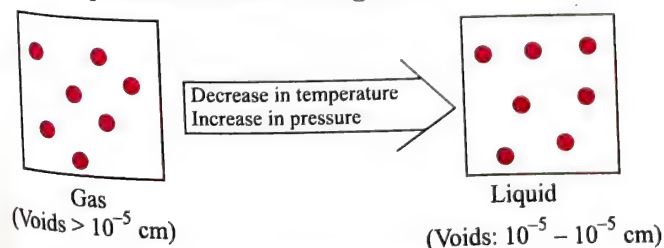


Fig. 5.30 Liquefaction of gases

5.16 CONCEPT OF CRITICAL CONSTANTS (ANDREW ISOTHERM)

In the previous section, we studied that a gas can be liquefied both by decreasing temperature and by increasing pressure. For example, sulphur dioxide can be liquefied at 265 K if pressure is 1 atm. It can also be liquefied at 293 K if the pressure is increased to 3.25 atm.

The effect of temperature, however, is more significant than pressure. This was proved by Thomas Andrew (1861) who studied the effect of temperature and pressure on a volume of CO_2 gas. He measured the volumes of carbon dioxide at different pressures keeping the temperature constant in his experiments. The plots of P vs V at different temperatures (called *isotherms* of carbon dioxides) have been given in Fig. 5.31.

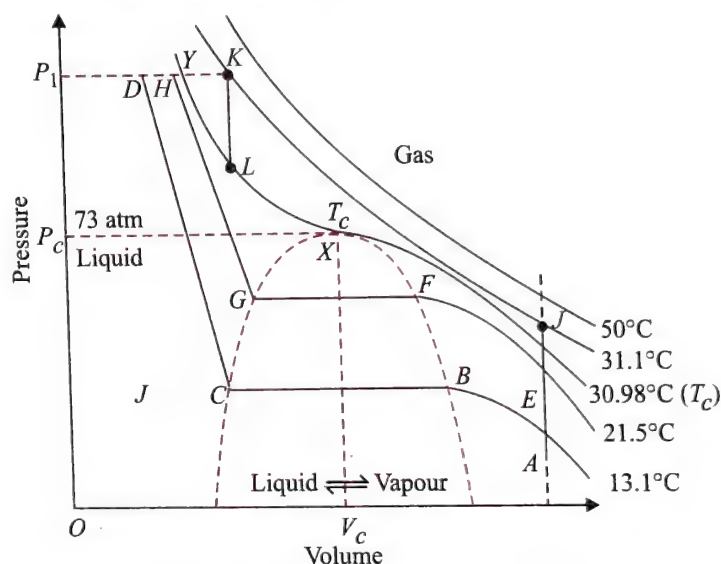


Fig. 5.31. Volume isotherms of carbon dioxide

At a low temperature (13.1°C, i.e., 286.2 K), CO_2 exists as gas at low pressure as shown by point A. As the pressure is increased, the volume of gas decreases along the curve AB. At point B, liquefaction starts. Hence, volume decreases rapidly along the line BC because a liquid has much less volume than a gas. At the point C, liquefaction is complete. Now a further increase in pressure has very little effect upon the volume because liquids are very less compressible. Hence, a steep curve CD is obtained as shown in the figure. Thus, along the portion AB, carbon dioxide exists only as gas, along the portion CD only as liquid and along the portion BC, the liquid and the vapour are in equilibrium with each other.

The isotherm EFGH at 21.5°C (294.6 K) is similar to that at 13.1°C (286.2 K) except that the horizontal portion over which the liquefaction occurs is shorter. In fact, as the temperature is raised, this portion becomes smaller and smaller (as indicated by the dotted boundary curve), and finally at 30.98°C (304.1 K), it is reduced only to a point. In the isotherms above 30.98°C (304.1 K), the horizontal portion completely disappears. This shows that above 30.98°C, the gas does not liquefy at all howsoever high pressure may be applied.

The point X is called the *critical point*, and the temperature corresponding to point X is called the *critical temperature*. The experimental study of carbon dioxide and other gases revealed that for every gas there is a certain temperature above which it cannot be liquefied howsoever high the pressure may be. The kinetic energy

of gas molecules above this temperature is sufficient enough to overcome the attractive forces. This temperature is referred to as *critical temperature* of the gas. The *critical temperature* of the gas may be defined as the temperature above which it cannot be liquefied by application of pressure. In other words, a gas remains in the gaseous state above its critical temperature. In order to liquefy it by compression, it has to be cooled to its critical temperature. Critical temperature is denoted by T_c . For example, T_c of CO_2 is $304.1 \text{ K} = 30.98^\circ\text{C}$.

Critical pressure (P_c): The pressure required to liquefy a gas at critical temperature is called critical pressure. For example, the value of P_c for CO_2 is 73.9 bar.

Critical volume (V_c): The volume of 1 mol of a gas at critical temperature and critical pressure is called critical volume. For example, the value of V_c for CO_2 is $94.0 \text{ cm}^3 \text{ mol}^{-1}$.

It may be noted that the parameters T_c , P_c , and V_c for a gas are collectively called *critical constants*.

At a high temperature (i.e., 50°C), the isotherms look like that of an ideal gas and no liquefaction occurs even if the pressure is very high (isotherm given at 50°C).

5.17 CONTINUITY OF STATE

In Fig. 5.31, end points of the horizontal lines have been connected by dots. This portion is known as *surface of discontinuity*. It separates the liquid state from the gaseous state. Within this curve, the liquid and the gas coexist. Because of this coexistence curve, it is possible to distinguish between the two states of matter, namely, gas and liquid. However, this is not always true in practice because it is possible to change a gas into liquid or a liquid into gas by a process in which always a single phase is present. For example, in Fig. 5.31 we can move from point A to J vertically by increasing the temperature. Then we can reach the point K by compressing the gas at a constant temperature along this isotherm (isotherm at 31.1°C). The pressure will increase. Now we can move vertically down towards L by lowering the temperature. As soon as we cross the point L on the critical isotherm, we get liquid. We end up with liquid, but in this series of changes, we do not pass through the two-phase region. If the process is carried out at the critical temperature, the substance always remains in one phase.

Thus, there is continuity between the gaseous and liquid states. The term fluid is used for either a liquid or a gas to recognise this continuity. Thus a liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface, there is no fundamental way of distinguishing between the two states. At the critical temperature, the liquid passes into gaseous state imperceptibly and continuously, and the surface separating the two phases disappears. A gas below the critical temperature can be liquefied by applying pressure and is called *vapour* of the substance. Carbon dioxide gas below its critical temperature is called carbon dioxide vapour. The critical constants for some common substances are given in Table 5.8.

Table 5.8 Critical constants for some substances

Substance	T_c (K)	P_c (bar)	V_c ($\text{dm}^3 \text{ mol}^{-1}$)
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Relationship between critical constant and van der Waals constants: The critical constants of a gas are related to its van der Waals constants as follows. These relations have been derived from the calculations based on the van der Waals equation.

a. $V_c = 3b$

b. $P_c = a/27b^2$

c. $T_c = 8a/27Rb$

d. The critical compressibility factor Z_c is given by

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{(a/27b^2)(3b)}{R[8a/27Rb]} \\ = \frac{a \times 3b \times 27Rb}{R \times 8a \times 27b^2} = \frac{3}{8} = 0.375$$

e. $T_c < T_b < T_i \left(\frac{8a}{27Rb} < \frac{a}{Rb} < \frac{2a}{Rb} \right) = \frac{8}{27} \quad 1:2=8:27:54$

Critical point: Critical point refers to the state of a substance at critical temperature and critical pressure. Some significant features are as follows:

- At the critical point, the density of the substance in gaseous and liquid states remains same.
- The surface of separation between liquid and gas disappears, and there is no distinction between liquid and gaseous states.
- No second phase is formed irrespective of the pressure of the system.
- Gases below their critical temperatures are called vapour.
- Fluids above critical temperature are called super critical fluids. Such fluids dissolve many organic substances. These are used for speedy separation of a mixture into its components. Carbon dioxide above 31.1°C and 600 bar pressure has a density around 1 g cm^{-3} and is used to remove caffeine from coffee beans instead of using chlorofluorocarbons, which are not environment friendly.

5.18 THE LAW OF CORRESPONDING STATES

Reduced equation of state: The van der Waals equation can be written in a form which does not contain any constant characteristic of individual gases. Such an equation is applicable to all gases. In order to obtain this equation, we need to define reduced pressure, and reduced volume as follows:

$$\text{Reduced pressure } (P_r) = \frac{P}{P_c}$$

$$\text{Reduced temperature } (T_r) = \frac{T}{T_c}$$

$$\text{Reduced volume } (V_r) = \frac{V}{V_c}$$

$$\text{Thus, } P = P_r P_c, T = T_r T_c, \text{ and } V = V_r V_c$$

Substituting these expressions of pressure (P), temperature (T), and volume (V) in the van der Waals equation.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

We get

$$\left(P_r P_c + \frac{a}{(V_r V_c)^2}\right)(V_r V_c - b) = RT_r T_c$$

We know that

$$P_c = \frac{a}{27b^2}, T_c = \frac{8a}{27Rb}, V_c = 3b$$

So on replacing P_c , V_c , and T_c in terms of a , b , and R ,

we get

$$\left\{P_r \frac{a}{27b^2} + \frac{a}{V_r^2 (3b)^2}\right\} \{V_r (3b) - b\} = RT_r \left(\frac{8a}{27Rb}\right)$$

$$\text{or } \left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \quad (i)$$

Equation (i) is known as the reduced equation of state. It does not contain any constant which is characteristic of a gas and, therefore, it is applicable to all gases.

According to the law of corresponding states, if two gases have the same values of reduced pressure and temperature, they will have the same reduced volume.

Relationship between Z and the reduced equation of state: The compressibility factor (Z) is PV_m/RT . Substituting P , V_m , and T in terms of reduced P_r , T_r , and V_r , we get

$$Z = \frac{PV_m}{RT}$$

$$= \frac{(P_r T_c)(V_r V_c)}{R(T_r T_c)} = \left(\frac{P_r V_c}{T_c}\right) \left(\frac{V_r}{T_c}\right)$$

$$\therefore \frac{P_r V_c}{T_c} = \frac{3}{8}$$

$$Z = \frac{3}{8} \frac{P_r V_r}{T_r} \quad \dots(ii)$$

The right-hand side of Eq. (ii) does not contain any constant and is independent of the nature of gas, and hence the value of Z is same for all gases.

5.19 LIQUID STATE

The liquid state is the intermediate state between the gaseous and solid states. The intermolecular forces are stronger in the liquid state than in the gaseous state. The molecules of liquids are held together by attractive intermolecular forces. They are so close that there is very little empty space between them, and under normal conditions, liquids are denser than gases. Liquids have definite

volume because their molecules do not separate from each other. However, the molecules can past one another freely. Therefore, liquids can be made to flow, can be poured, and can assume the shape of the container in which they are stored. This behaviour of liquids gives some characteristic properties such as definite volume but no definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

The characteristic properties of liquids are explained below.

5.19.1 PROPERTIES OF LIQUIDS

- Shape:** Liquids have no definite shape. They take up the shape of the vessel in which they are put. This is because their molecules are in a state of constant rapid motion.
- Volume:** Liquids have a definite volume. Their volumes do not depend upon the size or shape of the container. In liquids, the forces of attraction between the molecules are stronger and the molecules are closer to each other. Liquid molecules are not completely free to move.
- Density:** Liquids have much higher density than gases. In liquids, molecules are quite closely packed. Therefore, their densities are much higher than the densities of gases under comparable conditions. For example, the density of water at 373 K and 1 atm pressure is 0.958 g cm^{-3} , while that of water vapours at the same temperature and pressure is equal to $0.000588 \text{ g cm}^{-3}$.
- Compressibility:** Liquids are much less compressible than gases. This is because the space between the molecules of liquids is reduced almost to a minimum by intermolecular attraction. Therefore, liquids are much less compressible than gases.
- Diffusion:** Liquids diffuse like gases, but the diffusion is much slower. The slow diffusion in liquids can be explained in terms of smaller intermolecular spaces and restricted motion of molecules. Diffusion in liquids can be demonstrated by releasing a drop of ink in water. At first there is a sharp boundary between ink cloud and water. Eventually, the colour spreads uniformly throughout the water.
- Evaporation:** When a liquid is placed in an open vessel, its molecules constantly move in different directions with different velocities. Thus, as these molecules are moving with different speeds, they possess different kinetic energies. At any particular temperature, the energies of some molecules may be higher so that they can overcome the forces of attraction of the neighbouring molecules and can leave the liquid and come above the surface of the liquid. This process is called *evaporation*. Evaporation is a natural process. It occurs spontaneously at all temperatures.

Evaporation causes cooling: During evaporation, the molecules with higher kinetic energy get evaporated. The molecules remaining in the liquid state have lesser energy, and hence the temperature gets lower. This is the reason why evaporation causes cooling.

Factors affecting the rate of evaporation: The factors that affect the rate of evaporation are as follows:

- Temperature:** The rate of evaporation increases with an increase in temperature. At a higher temperature, the fraction

of molecules having sufficient kinetic energy to escape from the surface increases. This results in an increase in the rate of evaporation. Fig. 5.32 shows the change in evaporation with a rise in temperature.

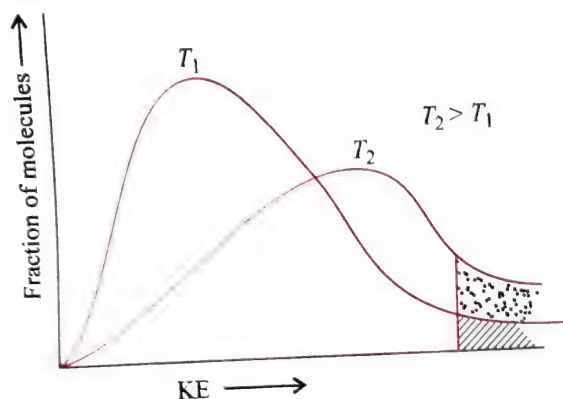


Fig. 5.32 Energy distribution graph

- b. **Surface area of liquid:** Evaporation is a surface phenomenon. High energy molecules from the liquid can go into the gaseous phase only through the surface. Therefore, the greater the surface area of the liquid, the greater the rate of evaporation.
- c. **Nature of liquid:** Liquids having weaker intermolecular forces of attraction can easily pass into the gaseous phase from the liquid phase. Therefore, the rate of evaporation is higher in such liquids. For example, dimethyl ether evaporates at a much faster rate than ethyl alcohol. A liquid which evaporates more readily is described as being more volatile.

5.19.2 VAPOUR PRESSURE

If a liquid is placed in a closed vessel, its molecules may go into the gaseous phase from the liquid phase due to evaporation.

As time passes, more and more molecules leave the liquid and come above the surface of the liquid. The molecules present above the liquid surface are called *vapours*. These molecules in the vapour phase are also constantly moving, and some of them strike the surface of the liquid, which may be recaptured by the liquid. The process is called *condensation*.

In the beginning, the rate of evaporation is high. However, as more and more molecules with higher energy leave the liquid, the rate of evaporation decreases with time. On the other hand, as the number of molecules in the vapour phase is very small in the beginning, the rate of condensation is very low. However, with the passage of time, as the number of molecules in the vapour phase increases, the rate of condensation also increases (Fig. 5.33). Ultimately, a stage is reached when the rate of evaporation becomes equal to the rate of condensation, i.e., equal number molecules leave and re-enter the liquid at the same time.

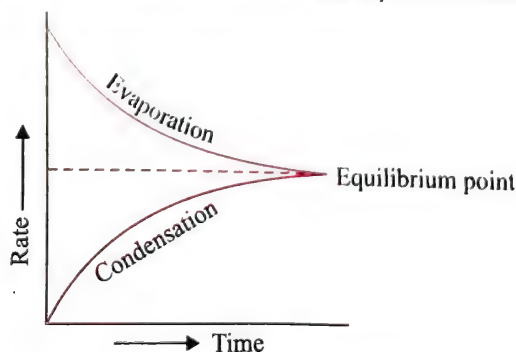


Fig. 5.33(a) Attainment of equilibrium

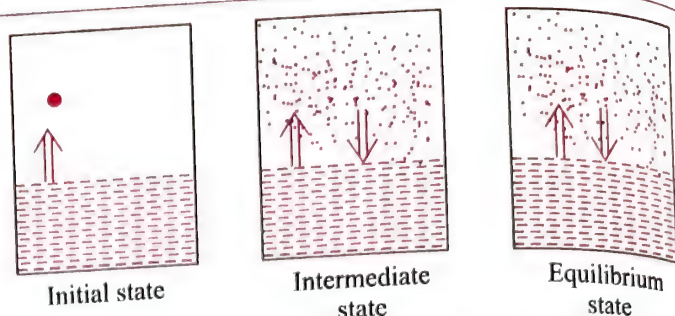


Fig 5.33(b) Diagrammatic presentation of attainment of equilibrium
(Liquid \rightleftharpoons Gas)

This state is called the state of equilibrium. The pressure exerted by the vapour at this stage (as indicated by a manometer) is called the vapour pressure. It is sometimes called the saturated vapour pressure because the vapour phase is saturated with vapour at this stage.

Hence, the vapour pressure of a liquid at any temperature is defined as the pressure exerted by the vapours in equilibrium with the liquid at that temperature.

The vapour pressure of a liquid depends upon the following factors:

- a. **Nature of liquids:** More volatile liquids have higher vapour pressures.
- b. **Temperature:** As temperature increases, the vapour pressure increases because at higher temperatures, larger number of molecules escape into the vapour phase. The vapour pressures of some common liquids at various temperatures are given in Fig. 5.34.

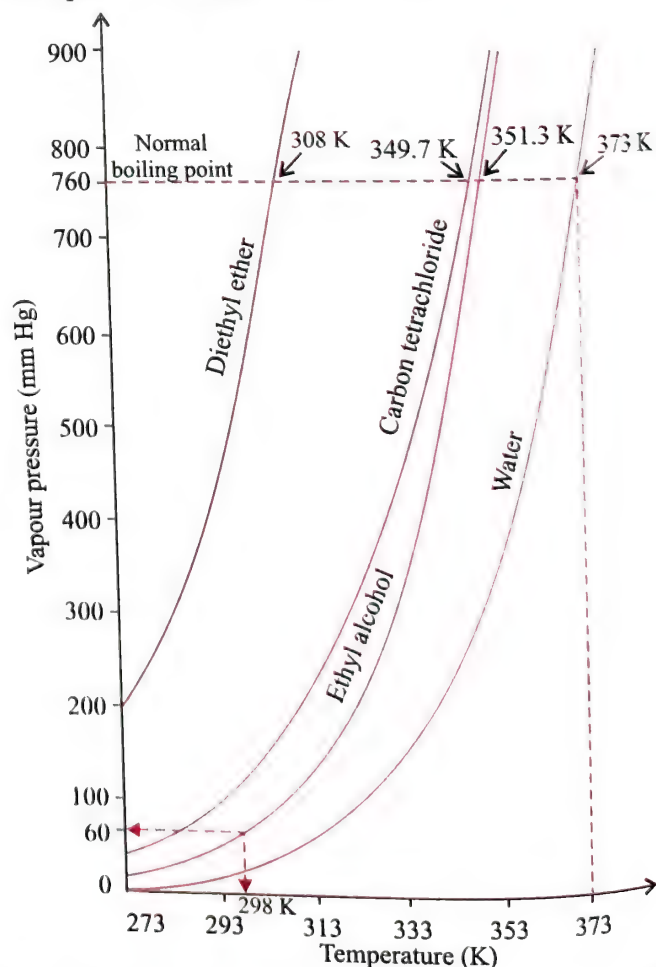


Fig. 5.34 Vapour pressure versus temperature curve of some common liquids

Boiling: Boiling is a special case of evaporation. It is the rapid conversion of a liquid into vapour.

bubbles. During boiling, evaporation is not restricted to the surface only but takes place throughout the bulk of the liquid.

The process of boiling can be understood as follows:

When a liquid is heated in an open vessel (Fig. 5.35), the liquid vapourises from the surface. At the temperature at which the vapour pressure of the liquid becomes equal to the external pressure, vapourisation occurs throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the boiling temperature at that pressure. At 1 atm pressure, the boiling temperature is called *normal boiling point*. If the pressure is 1 bar, then the boiling point is called *standard boiling point* of the liquid. The standard boiling point of a liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100°C (373 K); its standard boiling point is 99.6°C (372.6 K).

At high altitudes, atmospheric pressure is low. Therefore, liquids at high altitudes boil at lower temperatures in comparison to that at the sea level. Since water boils at a lower temperature on hills, a pressure cooker is used for cooking food. In hospitals, surgical instruments are sterilised in autoclaves in which the boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when a liquid is heated in a closed vessel. On heating continuously, vapour pressure increases. At first a clear boundary is visible between liquid and vapour phases because the liquid is denser than vapour. As the temperature increases, more and more molecules go into vapour phase and the density of vapours rises. At the same time, the liquid becomes less dense. It expands because molecules move apart. When the densities of the liquid and vapours become same, the clear boundary between them disappears. This temperature is called *critical temperature* about which we have already discussed.

Difference between boiling and evaporation: Both boiling and evaporation involve conversion of liquid into vapours and appear to be similar. However, they differ in some respect. The differences are listed below:

Table 5.9 Difference between boiling and evaporation

Evaporation	Boiling
a. Evaporation occurs at the surface of a liquid.	a. It involves the formation of bubbles even below the surface within the bulk of the liquid.
b. It occurs spontaneously at all temperatures.	b. It occurs only at a specific temperature at which the vapour pressure equals the imposed pressure on the liquid surface.
c. It is a slow phenomenon.	c. It is a rapid phenomenon.

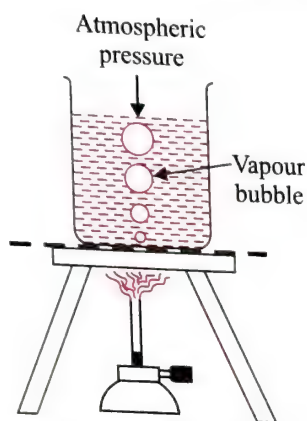


Fig. 5.35 Boiling of a liquid

Heat of vapourisation or enthalpy of vapourisation ($\Delta_{\text{vap}}H$): The amount of enthalpy required to convert a liquid into gas at a constant temperature is known as the enthalpy of vapourisation. **Molar enthalpy of vapourisation ($\Delta_{\text{vap}}H$)** is defined as the amount of enthalpy required to convert 1 mol of a liquid to gas at the boiling point of the liquid.

The greater the intermolecular forces of attraction present in a liquid, the greater the enthalpy of vapourisation and the higher the boiling point. For example, the enthalpy of vapourisation and boiling point of water are more than those of ether, acetone, benzene, etc.

5.20 SURFACE TENSION

This property of liquids is related to the strength of interparticle forces. A molecule well within the bulk of a liquid is uniformly attracted in all directions by the neighbouring molecules.

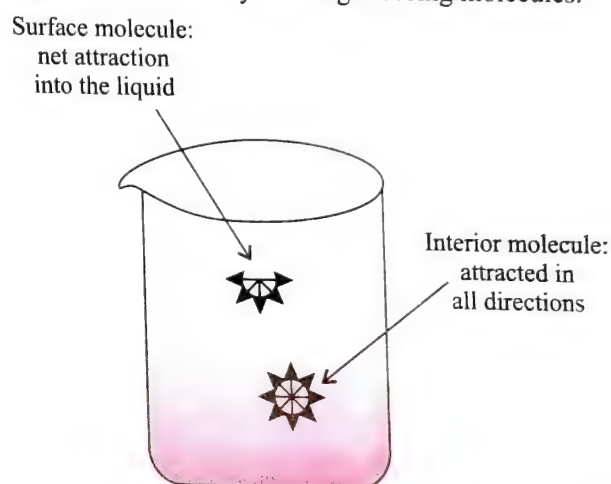


Fig. 5.36 Forces acting on a molecule on the surface and on a molecule inside the liquid

The net force of attraction acting on such a molecule is almost zero. A molecule at the surface of the liquid has no upper molecules to participate in attraction. This creates an imbalance of forces at the surface as shown in Fig. 5.36. Consequently, the molecules at the surface experience a resultant inward pull and the surface behaves as if it were a stretched membrane or were under tension. For a plane surface, the force acting parallel to the surface and perpendicular to a line of unit length anywhere in the surface is called *surface tension*. It is represented by a Greek letter gamma, γ , and is expressed in the units of dynes cm^{-1} or newton per meter (N m^{-1}).

In terms of dimensions,

Surface energy = work per sq cm = (force \times length) per sq. cm

$$= \frac{\text{dynes} \times \text{cm}}{\text{cm}^2} = \text{dynes cm}^{-1}$$

Due to surface tension, the molecules tend to leave the surface, and the surface of a liquid tends to minimise the surface area as far as possible. In order to increase the surface area of the liquid, some energy has to be supplied against the inward pull. This is referred to as **surface energy**.

Thus, surface energy is the energy required or work required to be done to increase the surface area of the liquid by a unit amount. It is expressed in J m^{-2} or N m^{-1} . [$\text{J m}^{-2} = \text{Nm (m}^{-2}) = \text{Nm}^{-1}$]. It may be noted that surface tension and surface energy have same dimensions.

Effect of temperature on surface tension: The magnitude of the surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. An increase in temperature increases the kinetic energy of the molecules, and the effectiveness of intermolecular attraction decreases. So the surface tension decreases as the temperature is raised.

The effect of temperature on surface tension is given by an equation deduced by Eotvas.

$$\gamma = k(T_c - T) \left(\frac{d}{M} \right)^{2/3}$$

Here, γ is the surface tension, k is the constant, d is density, M is molecular mass, T_c is the critical temperature, and T is temperature.

Evidently as T approaches the critical temperature, the surface tension becomes zero. At this stage, the meniscus between the liquid and vapours disappears.

Effect of adding surface active solutes: The addition of surface active solutes to a liquid also lowers the surface tension. For example, the addition of ethanol, soaps, detergents, etc., to water lowers its surface tension. The cleansing action of soap is based on this fact.

Some effects of surface tension: Let us now study some important phenomena that can be explained by surface tension:

- a. **Spherical shape of drops:** Surface tension causes liquid drops (or gas bubbles) to acquire spherical shape. This is because the lowest energy state of a liquid is attained when the surface area is minimum. Spherical shape satisfies this condition; that is why mercury drops are spherical in shape. This is why sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass. For a given volume, the sphere has a minimum surface area, as shown in Fig 5.37.

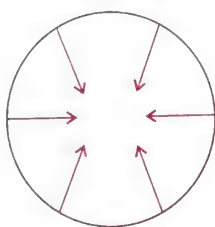


Fig. 5.37 Spherical structure of a liquid drop due to surface tension

- b. **Capillary action:** The surface tension of a liquid depends upon the forces between the molecules of the liquid. The attractive forces between the molecules of the same substance are called cohesive forces, while that in the molecules of different substances are called *adhesive forces*. When water is taken in a glass tube (such as burette), there are cohesive forces between water molecules and adhesive forces between glass and water. In this case, the adhesive forces are stronger than cohesive forces. As a result, water acquires a concave upward surface [see Fig. 5.38(a)]. Such a curved surface of a liquid is known as *miniscus*. In case of mercury, cohesive forces are stronger than adhesive forces, and hence mercury has concave downward miniscus [see Fig. 5.38 (b)]. The rise or fall of liquids in capillary tubes (known as capillary action) can also be explained in terms of surface tension.

etc., flow slowly, whereas others such as water, petrol, ethanol, etc., flow rapidly. This means that every liquid has some internal resistance to flow, which is referred to as *viscosity*. Liquids which flow slowly are said to be more viscous than the liquids which flow rapidly

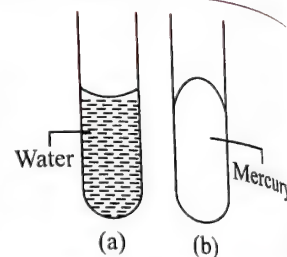


Fig. 5.38 Capillary action

Viscosity is a measure of resistance to flow arising due to the internal friction between layers of fluid as they slip past one another when the liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

To understand the nature of internal resistance or friction existing within a liquid, consider a liquid flowing through a narrow tube. All parts of the liquid do not move through the tube with the same velocity. Imagine

the liquid to be made up of a large number of thin cylindrical coaxial layers. The layer in contact with the walls of the tube is almost stationary.

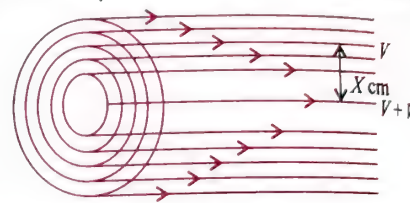


Fig. 5.39 Flow through a narrow tube

When a liquid flows over a fixed surface, the layer of molecules in immediate contact with the surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid (Fig. 5.40), the layer above it accelerates its flow and the layer below it retards its flow.

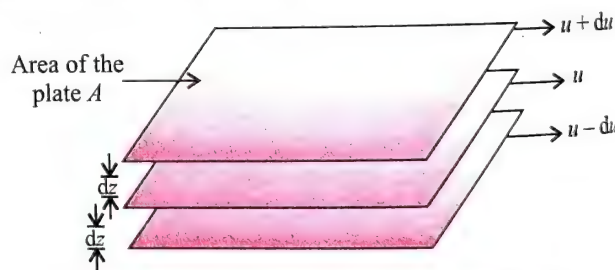


Fig. 5.40 Gradation of velocity in laminar flow

If the velocity of the layer at a distance dz is changed by a value du , then the velocity gradient is given by the amount du/dz . A force is required to maintain the flow of layers. This force is proportional to the area of contact of the layers and the velocity gradient, i.e.,

$$F \propto A \text{ (A is the area of contact)}$$

$$F \propto \frac{du}{dz}$$

where du/dz is the velocity gradient, the change in velocity with distance.

$$F \propto A \cdot \frac{du}{dz}$$

$$\Rightarrow F = \eta A \frac{du}{dz}$$

5.21 VISCOSITY

It is one of the characteristic properties of liquids. It is a well-known fact that some liquids such as honey, castor oil, glycerine,

η is the proportionality constant and is called *coefficient of viscosity*.

Now, if $A = 1 \text{ cm}^2$, $u = 1 \text{ cm s}^{-1}$, and $Z = 1 \text{ cm}$, then $F = \eta$.

Thus, coefficient of viscosity may be defined as the force of friction required to maintain the velocity difference of 1 cm s^{-1} between two parallel layers 1 cm apart and having an area of 1 cm^2 .

Units of viscosity: Units of viscosity are $\text{dyn cm}^{-2} \text{ s}$. This quantity is also called *1 poise* (after the name of Poiseuille). However, the SI units of viscosity are $\text{N m}^{-2} \text{ s}$ or $\text{kg m}^{-1} \text{ s}$

$$\text{Poise} = \text{gm cm}^{-1} \text{ s}$$

Poise is $1/10$ of SI unit.

Effect of temperature: With an *increase* in temperature, the magnitude of interparticle forces decreases and the kinetic energy of molecules increases. This causes a *decrease* in the viscosity of the liquid.

ILLUSTRATION 5.1 QS

- Why liquids have a definite volume but no definite shape?
- At a particular temperature why is the vapour pressure of acetone less than that of ether?
- A liquid is transferred from a smaller vessel to a bigger vessel at the same temperature. What will be the effect on the vapour pressure?
- Why vegetables are cooked with difficulty at a hill station?
- What is the approximate relationship between the heat of vapourisation and the boiling point of a liquid?
- What is the effect of temperature on surface tension and viscosity?
- Why are falling liquid drops spherical?
- Why liquids diffuse slowly as compared to gases?
- What is the binding force between molecules if a substance is a gas under ordinary conditions of temperature and pressure?

- This is because the intermolecular forces are strong enough to hold the molecules together but not strong enough to fix them into definite positions (as in solids). Instead, they possess fluidity, and hence, no definite shape.
- This is because the intermolecular forces of attraction in acetone are stronger than those present in ether.
- No effect as it depends only on the nature of the liquid and temperature.
- The atmospheric pressure is less and so the boiling point is lowered.
- $\Delta H_{\text{vap}} / T_b = 21 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Trouton's rule)
- Both decrease with increase in temperature.
- This is due to the property of surface tension possessed by liquids. This makes the surface area minimum. For a given volume, sphere has the minimum surface area.
- In liquids, the molecules are less free than in a gas, i.e., the intermolecular forces (van der Waals forces) in a liquid are greater than in a gas.
- van der Waals forces

CONCEPT APPLICATION EXERCISE 5.1

Subjective Type

- Write the kinetic gas equation and express it as $P = \frac{2}{3} E$, where E is the kinetic energy per unit volume.
- Calculate root mean square speed (rms) of ozone which is kept in a closed vessel at 20°C and a pressure of 82 mm of Hg.
- The density of steam at 100°C and 10^5 Pa pressure is 0.6 K gm^{-3} . Calculate the compressibility factor of the system.
- 2.0 mol of chlorine gas occupies a volume of 800 mL at 300 K and $5 \times 10^6 \text{ Pa}$ pressure. Calculate the compressibility factor of the gas ($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$). Comment whether the gas is more compressible or less compressible under these conditions.
- Calculate the pressure of 150 g carbon dioxide in a vessel of 2.0 L capacity at 30°C , $a = 3.648 \text{ L bar atm K}^{-1} \text{ mol}^{-1}$, $b = 0.0427 \text{ L mol}^{-1}$
- When a tyre is pumped up rapidly, its temperature rises. Would you expect the same effect if air were an ideal gas?
- Can we use Boyle's law to calculate the volume of a real gas from its initial state to final state by an adiabatic expansion?
- Which postulate of kinetic theory can be used to justify Dalton's law of partial pressures?
- A porous cup is filled with H_2 gas at the atmospheric pressure and is connected to a thin glass tube in a vertical position. The second end of the tube is immersed in water below it. After some time, water rises in the glass tube. Explain giving reasons.
- What is the meaning of pressure of the gas?
- What is the difference between barometer and manometer?
- Based upon Boyle's law, draw the plot of P vs V and also PV vs P .
- If a plot of V vs $^\circ\text{C}$ at constant pressure is drawn, at what temperatures will it cut the volume and temperature axes?
- Why do we add 273 to the temperature while dealing with problems on gas equation?
- Give the relationship between the molar volume of a gas and its molar mass.
- What would happen if the molecular collisions are non-elastic?
- Which postulates of kinetic theory are invalid at low temperatures or high pressures?
- What is the relationship between three types of molecular speeds at a given temperature?
- In the plot of Z (compressibility factor) vs P , Z attains a value of unity at a particular pressure. What does it signify?
- Draw the plot of $\log P$ vs $\log V$ for Boyle's law.
- Draw the plot of $\log V$ vs $\log T$.
- Is it possible to cool the gas to 0 K ?
- What is the ratio of average molecular KE of CO_2 to that of SO_2 at 27°C ?
- Point out the difference between London dispersion forces and dipole-dipole forces.

25. Falling liquid drops are spherical. Why?
 26. What happens if a liquid is heated to the critical temperature of its vapour?
 27. Can a gas with $a = 0$ be liquefied?

ANSWERS

1. $P = \frac{2}{3}E$ 2. $u = 3.90 \times 10^4 \text{ cm s}^{-1}$
 3. $P = 0.967$ 4. $Z = 0.796$
 5. $P = 35.73 \text{ bar}$

6–27. Refer solutions.

Solved Examples

EXAMPLE 5.1

100 mL of hydrogen was confined in a diffusion tube and exposed to air, and at equilibrium, a volume of 26.1 mL of air was measured in the tube. Again, when 100 mL of CO_2 was placed in the same tube and exposed to air, 123 mL of air was measured in the tube at the equilibrium. Find the molecular weight of CO_2 .

Sol. In the first case, when 100 mL of H_2 is diffused, the volume of air diffused was 26.1 mL. Thus

$$\frac{\text{Rate of diffusion of } \text{H}_2}{\text{Rate of diffusion of air}} = \frac{100}{26.1} \quad \dots(i)$$

$$\frac{\text{Rate of diffusion of } \text{CO}_2}{\text{Rate of diffusion of air}} = \frac{100}{123} \quad \dots(ii)$$

From Eqs. (i) and (ii), we get

$$\frac{r_{\text{H}_2}}{r_{\text{CO}_2}} = \frac{123}{26.1} = \sqrt{\frac{M_{\text{CO}_2}}{M_{\text{H}_2}}}$$

$$\text{Molecular weight of } \text{CO}_2 = \frac{123 \times 123}{26.1 \times 26.1} = 2 = 44.42$$

EXAMPLE 5.2

A given volume of oxygen containing 20% by volume of ozone required 175 s to effuse when an equal volume of oxygen took 167 s only, under similar conditions. Find the density of ozone.

Sol. Density of O_2 – O_3 mixture can be found by Graham's law.

$$\therefore \frac{175}{167} = \sqrt{\frac{\text{Density of } \text{O}_2 + \text{O}_3 \text{ mixture}}{16}}$$

Relative density of (20% O_3 + O_2 mixture)

$$= \frac{175 \times 175 \times 16}{167 \times 167} = 17.57$$

Let the d of O_3 be x .

Combined d of O_2 – O_3 mixture is

$$\frac{16 \times 80}{100} + \frac{x \times 20}{100} = 17.57 \quad \therefore x = 23.85\%$$

EXAMPLE 5.3

A gas-filled freely collapsible balloon is pushed from the surface level of a lake to a depth of 100 m. Approximately what percentage of its original volume will the balloon finally have? Assume that the gas behaves ideally

Sol. Let the volume of balloon at the surface of the lake be V

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dyn cm}^{-1} \\ = 981 \times 1033.6$$

$$\text{Pressure at the depth of 100 m} \\ = 76 \times 13.6 \times 981 + 100 \times 100 \times 1 \times 981 \\ = 981 (76 \times 13.6 + 10000) \\ = 981 \times 11033.6$$

$$P_1 V_1 = P_2 V_2 \\ 981 \times 1033.6 \times V = 981 \times 11033.6 \times V_2$$

$$V_2 = \frac{1033.6}{11033.6} \times V \\ = \frac{1033.6 \times V}{11033.6 \times V} \times 100\% = 9.367\%$$

EXAMPLE 5.4

1 L of a gaseous mixture is effused in 5 min 11 s, while 1 L of oxygen takes 10 min. The gaseous mixture contains methane and hydrogen. Calculate

- The density of gaseous mixture.
- The percentage by volume of each gas in mixture.

Sol.

O_2	Mixture
$d_1 = 16$	$d_2 = ?$
$t_1 = 10 \times 60 = 600 \text{ s}$	$t_2 = 5 \times 60 + 11 = 311 \text{ s}$

 Volume is same, so

$$\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}}$$

$$\frac{311}{600} = \sqrt{\frac{d_2}{16}}$$

$$\Rightarrow \frac{(311)^2}{(600)^2} = \frac{d_2}{16}$$

$$\Rightarrow d_2 = 4.3$$

$$d_{\text{H}_2} = 1 \text{ and } d_{\text{CH}_4} = 8. \text{ So}$$

$$d_{\text{mix}} = \frac{d_{\text{CH}_4} \times x + (100 - x)d_{\text{H}_2}}{100}$$

$$4.3 \times 100 = 8x + (100 - x) \times 1$$

$$430 = 8x + 100 - x$$

$$330 = 7x$$

$$x = 47.14\%$$

$$\% \text{CH}_4 = 47.14, \% \text{H}_2 = 52.86$$

EXAMPLE 5.5

Two flasks A and B have equal volumes. Flask A containing H_2 gas is maintained at 27°C while B containing an equal mass of C_2H_6 gas is maintained at 627°C . In which flask and by how many times are molecules moving faster, assuming ideal behaviour for both the gases?

Sol. Calculate the relative velocities of molecules.

Average velocity of a gas

$$\mu = \sqrt{\frac{8RT}{\pi M_w}}$$

$$\mu_{H_2} = \sqrt{\frac{8RT_1}{\pi M_1}}, \mu_{C_2H_6} = \sqrt{\frac{8RT_2}{\pi M_2}}$$

$$\frac{\mu_{H_2}}{\mu_{C_2H_6}} = \sqrt{\frac{T_1 M_2}{T_2 M_1}} \quad [T_1 = 300 \text{ K}, T_2 = 900 \text{ K}]$$

$$M_1 = 2 \text{ g mol}^{-1}$$

$$M_2 = 30 \text{ g mol}^{-1}$$

$$\frac{\mu_{H_2}}{\mu_{C_2H_6}} = \sqrt{\frac{300 \times 30}{900 \times 2}} = \frac{\sqrt{5}}{1} = 2.237:1$$

Thus, H_2 molecules in flask A will be moving 2.237 times faster than C_2H_6 molecules in B.

EXAMPLE 5.6

Calculate the pressure exerted by one mole of CO_2 gas at 273 K if the van der Waals constant $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$. Assume that the volume occupied by CO_2 molecules is negligible.

Sol. The van der Waals equation for one mole of a gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

It is given that the volume occupied by CO_2 molecules is negligible. Hence, the equation of state becomes

$$\left(p + \frac{a}{V^2}\right)(V) = RT$$

$$\text{or } p = \frac{RT}{V} - \frac{a}{V^2}$$

Assuming $V_m = 22.414 \text{ dm}^3 \text{ mol}^{-1}$, we get

$$p = \frac{(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(273 \text{ K})}{(22.414 \text{ dm}^3 \text{ mol}^{-1})} - \frac{3.592 \text{ dm}^6 \text{ atm mol}^{-2}}{(22.414 \text{ dm}^3 \text{ mol}^{-1})^2}$$

$$= 101.246 \text{ kPa} - 7.15 \times 10^{-3} \text{ atm}$$

$$= 101.246 \text{ kPa} - (7.15 \times 10^{-3} \text{ atm}) \left(\frac{101.325 \text{ kPa}}{1 \text{ atm}}\right)$$

$$= 101.264 \text{ kPa} - 0.724 \text{ kPa}$$

$$= 100.601 \text{ kPa}$$

EXAMPLE 5.7

At a constant temperature, a gas occupies a volume of 200 mL at a pressure of 0.720 bar. It is subjected to an external pressure of 0.900 bar. What is the resulting volume of the gas?

Sol. Boyle's law is applicable as the amount and temperature are unaltered

$$p_1 V_1 = p_2 V_2$$

$$\text{or } p_1/p_2 = V_2/V_1$$

substituting the values, we get

$$0.720 \text{ bar}/0.900 \text{ bar} = V_2/200 \text{ mL}$$

$$V_2 = \frac{720}{900} \times 200 \text{ mL} = 160 \text{ mL}$$

Boyle's law is manifested in the working of many devices used in daily life such as cycle pump, aneroid barometer and type pressure gauge, etc.

EXAMPLE 5.8

What is the increase in volume when the temperature of 600 mL of air increases from 27°C to 47°C under constant pressure?

Sol. Charles' law is applicable as the pressure and amount remains constant.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } V_1 = \frac{T_1}{T_2} \times V_2$$

$$V_1 = \frac{320 \text{ K}}{300 \text{ K}} \times 600 \text{ mL} = 640 \text{ mL}$$

Increase in volume of air is

$$640 \text{ mL} - 600 \text{ mL} = 40 \text{ mL}$$

EXAMPLE 5.9

A 2.5 L flask contains 0.25 mol each of sulphur dioxide and nitrogen gas at 27°C . Calculate the partial pressure exerted by each gas and also the total pressure.

Sol. Partial pressure of sulphur dioxide.

$$\begin{aligned} p_{SO_2} &= nRT/V \\ &= \frac{0.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \times 300 \text{ K}}{2.5 \times 10^{-3} \text{ m}^3} \\ &= 2.49 \times 10^5 \text{ N m}^{-2} = 2.49 \times 10^5 \text{ Pa} \end{aligned}$$

Similarly, $p_{N_2} = 2.49 \times 10^5 \text{ Pa}$

Following Dalton's law, we get

$$\begin{aligned} p_{\text{Total}} &= p_{N_2} + p_{SO_2} \\ &= 2.49 \times 10^5 \text{ Pa} + 2.49 \times 10^5 \text{ Pa} \\ &= 4.98 \times 10^5 \text{ Pa} \end{aligned}$$

EXAMPLE 5.10

Which of the two gases, ammonia and hydrogen chloride, will diffuse faster and by what factor?

$$\begin{aligned} \text{Sol. } r_{NH_3}/r_{HCl} &= (M_{HCl}/M_{NH_3})^{1/2} \\ &= (36.5/17)^{1/2} = 1.46 \end{aligned}$$

$$\text{or } r_{NH_3} = 1.46 r_{HCl}$$

Thus, ammonia will diffuse 1.46 times faster than hydrogen chloride gas.

EXAMPLE 5.11

What volume of air will be expelled from a vessel containing 400 cm^3 at 7°C when it is heated to 27°C at the same pressure?

$$\text{Sol. } \frac{V_1}{T_1} = \frac{V_2}{T_2},$$

$$\text{i.e., } \frac{400 \text{ cm}^3}{(273 + 7) \text{ K}} = \frac{V_2}{(273 + 27) \text{ K}}$$

$$\text{or } V_2 = \frac{400}{280} \times 300 \text{ cm}^3 = 482.6 \text{ cm}^3$$

This is the volume after expansion. So

$$\text{volume expelled} = (482.6 - 400) \text{ cm}^3 = 82.6 \text{ cm}^3$$

EXAMPLE 5.12

Calculate the root mean square, average, and most probable speeds of H_2 molecules. The density of the gas at 101.325 kPa is 0.09 g dm^{-3} (0.09 kg m^{-3}). Assume ideal behaviour.

Sol. $u_{\text{RMS}} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3PV}{M_w}} = \sqrt{\frac{3P}{d}} = \left\{ \frac{3(101.325 \times 10^3 \text{ Pa})}{(0.09 \text{ kg m}^{-3})} \right\}^{1/2}$

$$= 1838 \text{ m s}^{-1}$$

$$u_{\text{AV}} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8PV}{\pi M_w}} = \sqrt{\frac{8P}{\pi d}} = \left\{ \frac{8(101.325 \times 10^3 \text{ Pa})}{3.14(0.09 \text{ kg m}^{-3})} \right\}^{1/2}$$

$$= 1694 \text{ m s}^{-1}$$

$$u_{\text{MP}} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2PV}{M_w}} = \sqrt{\frac{2P}{d}} = \left\{ \frac{2(101.325 \times 10^3 \text{ Pa})}{(0.09 \text{ kg m}^{-3})} \right\}^{1/2}$$

$$= 1501 \text{ m s}^{-1}$$

EXAMPLE 5.13

The van der Waals constant b of Ar is $3.22 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Calculate the molecular diameter of Ar.

Sol. Use $b = 4 \times$ volume occupied by the molecules in 1 mol of a gas

$$b = 4 \times N_0 \times \left(\frac{4}{3} \pi r^3 \right)$$

$$3.22 \times 10^{-5} = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$r = \left[\frac{3.22 \times 10^{-5} \times 3 \times 7}{4 \times 6.023 \times 10^{23} \times 4 \times 22} \right]^{1/3}$$

$$= 0.1472 \times 10^{-9} \text{ m} = 0.1472 \text{ nm}$$

$$d = 2r = 0.2944 \text{ nm}$$

EXAMPLE 5.14

1 mol of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If van der Waals constants are $a = 20.39 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.1383 \text{ L mol}^{-1}$, calculate compressibility factor Z under

- Low pressure region
- High pressure region

Sol.

- Under low pressure region, V is high

$$(V - b) \approx V$$

$$\left(P + \frac{a}{V^2} \right) V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\therefore Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV} \right)$$

$$= 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

- Under high pressure region, P is high

$$\left(P + \frac{a}{V^2} \right) V \approx P$$

$$\therefore P(V - b) = RT \quad \text{or} \quad PV - Pb = RT$$

$$\text{or } \frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\Rightarrow Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$= 1 + \frac{b}{V} \text{ by approximation } \left(\because \frac{PV}{RT} = 1, \frac{P}{RT} = \frac{1}{V} \right)$$

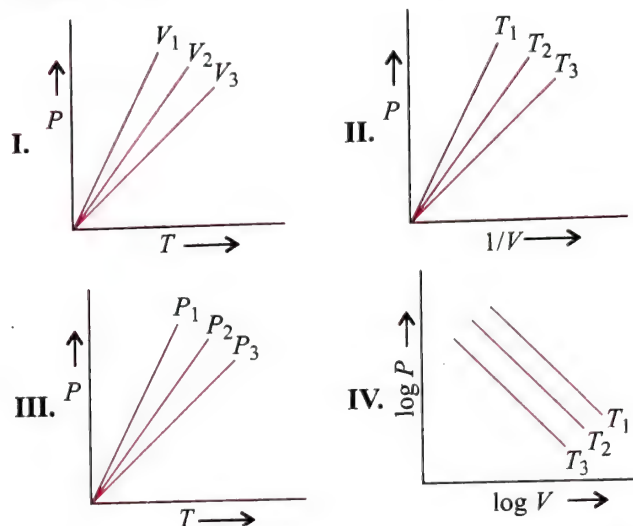
$$= 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

Single Correct Answer Type

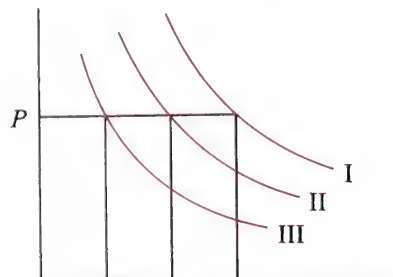
- A quantity of heat is confined in a chamber of constant volume. When the chamber is immersed in a bath of melting ice, the pressure of the gas is 1000 torr. Final temperature when the pressure manometer indicates an absolute pressure of 400 torr is
(1) 109 K (2) 273 K (3) 373 K (4) 0 K
- At what temperature will both celsius and fahrenheit scales read the same value?
(1) 100° (2) 180° (3) 40° (4) -40°
- At the top of the mountain, the thermometer reads 0°C and the barometer reads 710 mm Hg. At the bottom of the mountain the temperature is 30°C and the pressure is 760 mm Hg. The ratio of the density of air at the top with that at the bottom is
(1) 1:1 (2) 1.04:1
(3) 1:1.04 (4) 1:1.5
- A quantity of gas is collected in a graduated tube over the mercury. The volume of the gas at 20°C is 50.0 mL and the level of the mercury in the tube is 100 mm above the outside mercury level. The barometer reads 750 mm. Volume at STP is
(1) 39.8 mL (2) 40 mL
(3) 42 mL (4) 60 mL
- Which of the following contains greatest number of N atoms?
(1) 22.4 L nitrogen gas at STP
(2) 500 mL of 2.00 M NH₃
(3) 1.00 mol of NH₄Cl
(4) 6.02×10^{23} molecules of NO₂
- What weight of hydrogen at STP could be contained in a vessel that holds 4.8 g oxygen at STP?
(1) 4.8 g (2) 3.0 g (3) 0.6 g (4) 0.3 g
- At moderate pressures, the van der Waals equation is written as
$$\left[P + \frac{a}{V^2}\right]V = RT$$

The compressibility factor is then equal to
(1) $\left(1 - \frac{a}{RTV}\right)$ (2) $\left(1 - \frac{RTV}{a}\right)$
(3) $\left(1 + \frac{a}{RTV}\right)$ (4) $\left(1 + \frac{RTV}{a}\right)$
- Ideal gas equation in terms of KE per unit volume, E , is
(1) $\frac{3}{2}RT$ (2) $\frac{2}{3}E$ (3) $\frac{2}{3}RT$ (4) $\frac{3}{2}E$

9. For 1 mol of an ideal gas, $V_1 > V_2 > V_3$ in Fig. (I), $T_1 > T_2 > T_3$ in Fig. (II), $P_1 > P_2 > P_3$ in Fig. (III), and $T_1 > T_2 > T_3$ in Fig. (IV), then which curves are correct.



- (1) I, II (2) I, II, III (3) II, IV (4) I, III, IV
10. I, II, and III are three isotherms, respectively, at T_1 , T_2 , and T_3 . Temperature will be in order



- (1) $T_1 = T_2 = T_3$ (2) $T_1 < T_2 < T_3$
(3) $T_1 > T_2 > T_3$ (4) $T_1 > T_2 = T_3$
11. A quantity of hydrogen gas occupies a volume of 30.0 mL at a certain temperature and pressure. What volume would half this mass of hydrogen occupy at triple the absolute temperature if the pressure were one-ninth that of the original gas?
(1) 270 mL (2) 90 mL (3) 405 mL (4) 137 mL
12. A gas in an open container is heated from 27°C to 127°C. The fraction of the original amount of the gas remaining in the container will be
(1) 3/4 (2) 1/2 (3) 1/4 (4) 1/8
13. The density of neon gas will be highest at
(1) STP (2) 0°C, 2 atm
(3) 273°C, 1 atm (4) 273°C, 2 atm
14. A mixture of SO₂ and O₂ in the molar ratio 16 : 1 is diffused through a pin hole for successive effusions three times to give a molar ratio 1 : 1 of diffused mixture. Which one are not correct if diffusion is made at same P and T in each operation?

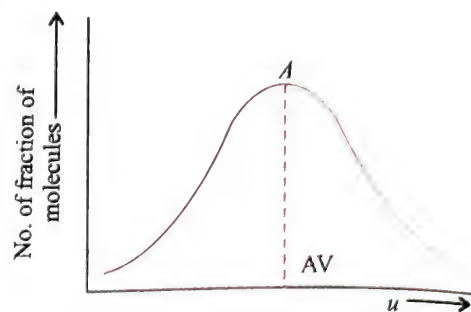
- I. Eight operation are needed to get 1 : 1 molar ratio.
II. Rate of diffusion for SO₂ : O₃ after eight operations in 0.707.

- III. Six operations are needed to get 2 : 1 molar ratio for SO_2 and O_2 in diffusion mixture.
- IV. Rate of diffusion for SO_2 and O_2 after six operations is 2.41.
- (1) I, II, III (2) II, III
(3) I, III (4) IV
15. A graph is plotted between $\log V$ and $\log T$ for 2 mol of gas at constant pressure of 0.0821 atm. V and T are in litre and K. Which of the following statements are not correct?
- I. The curve is straight line with slope -1 .
II. The curve is straight line with slope $+1$.
III. The intercept on Y -axis is equal to 2.
IV. The intercept on Y -axis is equal to 0.3010.
- (1) I, II (2) III, IV (3) II, IV (4) I, III
16. A gas obeys $P(V - b) = RT$. Which of the following are correct about this gas?
- I. Isochoric curves have slope $= \frac{R}{V - b}$.
II. Isobaric curves have slope $\frac{R}{P}$ and intercept b .
III. For the gas compressibility factor $= 1 + \frac{Rb}{RT}$.
IV. The attraction forces are overcome by repulsive forces.
- (1) I (2) II, III (3) III (4) I, II, III, IV
17. The pressure of real gas is less than the pressure of an ideal gas because of
- (1) Increase in collisions
(2) Increase in intermolecular forces
(3) Infinite size of molecules
(4) Statement is incorrect
18. O_2 gas at STP contained in a flask was replaced by SO_2 under same conditions. The weight of SO_2 will be
- (1) Equal to that of O_2 (2) Half that of O_2
(3) Twice that of O_2 (4) One-fourth of O_2
19. At what temperature will hydrogen molecules have the same KE as nitrogen molecules at 280 K?
- (1) 280 K (2) 40 K (3) 400 K (4) 50 K
20. Select the correct statement.
- I. Greater is humidity, lesser will be rate of evaporation of water.
II. Greater is the humidity, lesser will be density of air.
III. If room temperature = dew point, relative humidity = 100%.
IV. Dew point is the temperature at which the gas at a given atmospheric condition becomes saturated with H_2O (v).
- (1) I, II (2) II, IV (3) All (4) None
21. The temperature to which a gas must be cooled before it can be liquefied by compression is called
- (1) Boyle's temperature
(2) Critical temperature

(3) Liquefaction temperature

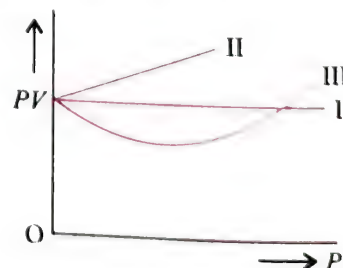
(4) Inversion temperature

22. Distribution of molecules with velocity is represented by the curve



Velocity corresponding to point A is

- (1) $\sqrt{\frac{3RT}{M_w}}$ (2) $\sqrt{\frac{2RT}{M_w}}$ (3) $\sqrt{\frac{8RT}{\pi M_w}}$ (4) $\sqrt{\frac{RT}{M_w}}$
23. The volume of helium is 44.8 L at
- (1) 100°C and 1 atm (2) 0°C and 1 atm
(3) 0°C and 0.5 atm (4) 100°C and 0.5 atm
24. Which gas shows real behaviour?
- (1) 8 g O_2 at STP occupies 5.6 L.
(2) 1 g H_2 in 0.5 L flask exerts a pressure of 24.63 atm at 300 K.
(3) 1 mol NH_3 at 300 K and 1 atm occupies volume 22.4 L.
(4) 5.6 L of CO_2 at STP is equal to 11 g.
25. For the non-zero volume of the molecules, real gas equation for n mol of the gas will be
- (1) $\left(P + \frac{a}{V^2}\right)V = RT$
(2) $PV = nRT + nbP$
(3) $P(V - nb) = nRT$
(4) Both (2) and (3) are true.
26. Actual graph for the given parameters in (Q. 25) will be



- (1) I, III (2) I, II (3) II (4) I
27. For the non-zero value of the force of attraction between gas molecules, gas equation will be
- (1) $PV = nRT - \frac{n^2a}{V}$ (2) $PV = nRT + nbP$
(3) $PV = nRT$ (4) $P = \frac{nRT}{V - b}$
28. If χ_M , χ_P , and χ_V are mole fraction, pressure fraction and volume fraction respectively of a gaseous mixture, then:

$$(1) \chi_M = \frac{1}{\chi_P} = \frac{1}{\chi_V}$$

$$(2) \frac{1}{\chi_M} = \chi_P = \frac{1}{\chi_V}$$

$$(3) \chi_M = \chi_P = \chi_V$$

$$(4) \frac{1}{\chi_P} = \frac{1}{\chi_M} = \frac{1}{\chi_V}$$

29. The average molecular speed is greatest in which of the following gas samples?

- (1) 1.0 mol N_2 at 560 K
(2) 0.50 mol of Ne at 500 K
(3) 0.20 mol of CO_2 at 440 K
(4) 2.0 mol of Ke at 140 K

30. A gas in an open container is heated from $27^\circ C$ to $127^\circ C$. The fraction of the original amount of the gas escaped in the container will be

- (1) $3/4$ (2) $1/2$ (3) $1/4$ (4) $1/8$

31. Virial equation is: $PV_M = RT \left[A + \frac{B}{V_M} + \frac{C}{V_M^2} + \dots \right]$,

where A, B, C, \dots are first second, third, ... virial coefficient, respectively. For an ideal gas.

- (1) A = unity and B, C are zero.
(2) A, B, C are all equal to unity.
(3) A is dependent of temperature.
(4) All A, B, C depend on temperature.

32. A balloon filled with ethyne is pricked with a sharp point and quickly dropped in a tank of H_2 gas under identical conditions. After a while the balloon will

- (1) Shrink
(2) Enlarge
(3) Completely collapse
(4) Remain unchanged in size

33. A flask containing 12 g of a gas of relative molecular mass 120 at a pressure of 100 atm was evacuated by means of a pump until the pressure was 0.01 atm. Which of the following is the best estimate of the number of molecules left in the flask ($N_0 = 6 \times 10^{23} \text{ mol}^{-1}$)?

- (1) 6×10^{19} (2) 6×10^{18} (3) 6×10^{17} (4) 6×10^{13}

34. For an ideal gas, the value of compressibility factor

$$Z = \left(\frac{pV_m}{RT} \right) \text{ is}$$

- (1) 0 (2) 1
(3) > 1 (4) Between 0 and 1

35. NH_3 gas is liquefied more easily than N_2 . Hence

- (1) van der Waals constants a and b of $NH_3 >$ that of N_2
(2) van der Waals constants a and b of $NH_3 <$ that of N_2
(3) $a(NH_3) > a(N_2)$ but $b(NH_3) < b(N_2)$
(4) $a(NH_3) < a(N_2)$ but $b(NH_3) > b(N_2)$

36. The van der Waals equation for one mol of CO_2 gas at low pressure will be

$$(1) \left(P + \frac{a}{V^2} \right) V = RT \quad (2) P(V - b) = RT - \frac{a}{V^2}$$

$$(3) P = \frac{RT}{V - b}$$

$$(4) P = \left(\frac{RT}{V - b} - \frac{a}{V^2} \right)$$

37. If v is the volume of one molecule of a gas under given conditions, then van der Waals constant b is

- (1) $4v$ (2) $4v/N_0$
(3) $N_0/4v$ (4) $4vN_0$

38. Which of the following has the maximum value of mean free path?

- (1) CO_2 (2) H_2 (3) O_2 (4) N_2

39. The compressibility factor for definite amount of van der Waals' gas at $0^\circ C$ and 100 atm is found to be 0.5. Assuming the volume of gas molecules negligible, the van der Waals' constant a for a gas is

- (1) $1.256 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$ (2) $0.256 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$
(3) $2.256 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$ (4) $0.0256 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$

40. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

- (1) Fewer electrons than O_2
(2) Two covalent bonds
(3) V-shape
(4) Dipole moment

41. The pressure exerted by 1 mol of CO_2 at 273 K is 34.98 atm. Assuming that volume occupied by CO_2 molecules is negligible, the value of van der Waals' constant for attraction of CO_2 gas is

- (1) $3.59 \text{ dm}^6 \text{ atm mol}^{-2}$ (2) $2.59 \text{ dm}^6 \text{ atm mol}^{-2}$
(3) $1.25 \text{ dm}^6 \text{ atm mol}^{-2}$ (4) $1.59 \text{ dm}^6 \text{ atm mol}^{-2}$

42. Relative humidity of air is 60° and the saturation vapour pressure of water vapour in air is 3.6 kPa. The amount of water vapours present in 2 L air at 300 K is

- (1) 52 g (2) 31.2 g (3) 26 g (4) 5.2 g

43. A 3 : 2 molar mixture of N_2 and CO is present in a vessel at 500 bar pressure. Due to hole in the vessel, the gas mixture leaks out. The composition of mixture effusing out initially is

- (1) $n_{N_2} : n_{CO} :: 1 : 2$ (2) $n_{N_2} : n_{CO} :: 6 : 1$
(3) $n_{CO} : n_{N_2} :: 1 : 2$ (4) $n_{CO} : n_{N_2} :: 2 : 3$

44. Number of N_2 molecules present in L vessel at NTP when compressibility factor is 1.2 is

- (1) 2.23×10^{24} (2) 2.23×10^{22}
(3) 2.7×10^{22} (4) 2.7×10^{24}

45. A spherical air bubble is rising from the depth of a lake when pressure is P atm and temperature is T K. The percentage increase in the radius when it comes to the surface of a lake will be (Assume temperature and pressure at the surface to be, respectively, $2T$ K and $P/4$.)

- (1) 100% (2) 50% (3) 40% (4) 200%

46. When the temperature is increased, surface tension of water:

- (1) Increases
(2) Decreases
(3) Remains constant
(4) Shows irregular behaviour

47. Boltzmann constant (k) is given by

- (1) $k = R \times N_A$ (2) $k = 1.3807 \times 10^{-21} \text{ J K}^{-1}$
(3) $k = N_A/R$ (4) $k = R/N_A$

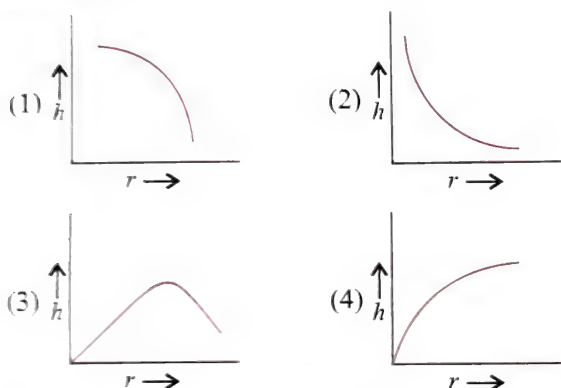
48. It is easier to liquefy oxygen than hydrogen because.

- (1) Oxygen has a higher critical temperature and lower inversion temperature than hydrogen.
- (2) Oxygen has a lower critical temperature and higher inversion temperature than hydrogen.
- (3) Oxygen has a higher critical temperature and higher inversion temperature than hydrogen.
- (4) The critical temperature and inversion temperature of oxygen is very low.

49. 2 mol H_2 is mixed with 2 gm of H_2 . The molar heat capacity at constant pressure for the mixture is

- (1) $\frac{17R}{6}$ (2) $\frac{11R}{6}$ (3) $4R$ (4) $\frac{3R}{2}$

50. Which of following correctly represents the relation between capillary rise h and capillary radius r ?



51. There is a depression in the surface of the liquid in a capillary when

- (1) The cohesive force is smaller than the adhesive force.
- (2) The cohesive force is greater than the adhesive force.
- (3) The cohesive and adhesive forces are equal.
- (4) None of the above is true.

52. Surface tension does not vary with

- (1) Temperature (2) Vapour pressure
- (3) The size of surface (4) Concentration

53. Which among of the following has least surface tension?

- (1) Benzene (2) Acetic acid
- (3) Diethyl ether (4) Chlorobenzene

54. The SI unit of the coefficient of viscosity is

- (1) $\text{N s}^{-1} \text{m}^{-1}$ (2) N s m^{-2}
- (3) $\text{N s}^{-2} \text{m}^{-2}$ (4) $\text{N s}^{-1} \text{m}^{-2}$

55. The quantity $(PV/K_B T)$ represents

- (1) Number of molecules in the gas
- (2) Mass of the gas
- (3) Number of moles of the gas
- (4) Translational energy of the gas

56. 1 of N_2 and $7/8$ L of O_2 at the same temperature and pressure were mixed together. what is the relation between the masses of the two gases in the mixture?

- (1) $M_{\text{N}_2} = 3M_{\text{O}_2}$ (2) $M_{\text{N}_2} = 8M_{\text{O}_2}$
- (3) $M_{\text{N}_2} = M_{\text{O}_2}$ (4) $M_{\text{N}_2} = 16M_{\text{O}_2}$

57. The value of PV for 5.6 L of an ideal gas is RT at NTP.

- (1) 0.25 (2) 0.30 (3) 1.0 (4) 0.45

58. If a gas is expanded at constant temperature

- (1) The pressure decreases
- (2) The kinetic energy of the molecules remains the same
- (3) The kinetic energy of the molecules decreases
- (4) The number of molecules of the gas increases

59. The density of a gas A is twice that of a gas B at the same temperature. The molecular mass of gas B is thrice that of A . The ratio of the pressure acting on A and B will be

- (1) 1 : 6 (2) 7 : 8 (3) 2 : 5 (4) 1 : 4

60. Which of the following expression at constant pressure represents Charles' law?

- (1) $V \propto \frac{1}{T}$ (2) $V \propto \frac{1}{T^2}$
- (3) $V \propto T$ (4) $V = d$

61. A gas of volume 100 cc is kept in a vessel at pressure 10.4 Pa maintained at temperature 24°C . Now, if the pressure is increased to 105 Pa, keeping the temperature constant, then the volume of the gas becomes

- (1) 10 cc (2) 100 cc
- (3) 1 cc (4) 1000 cc

62. A sample of gas occupies 100 mL at 27°C and 740 mm pressure. When its volume is changed to 80 mL at 740 mm pressure, the temperature of the gas will be

- (1) 21.6°C (2) 240°C
- (3) -33°C (4) 89.5°C

63. At 25°C and 730 mm pressure, 730 mL of dry oxygen was collected. If the temperature is kept constant what volume will oxygen gas occupy at 760 mm pressure?

- (1) 701 mL (2) 449 mL (3) 569 mL (4) 621 mL

64. The density of a gas at 27°C and 1 atm is d . Pressure remaining constant, at which of the following temperature will its density become $0.75d$?

- (1) 20°C (2) 30°C (3) 400 K (4) 300 K

65. The kinetic theory of gases predicts that total kinetic energy of a gaseous assembly depends on

- (1) Pressure of the gas
- (2) Temperature of the gas
- (3) Volume of the gas
- (4) Pressure, temperature, and volume of the gas

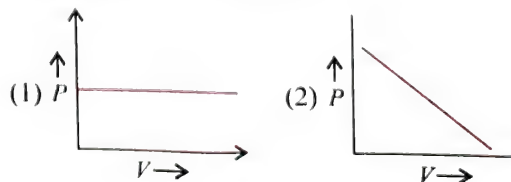
66. At STP, the order of mean square velocity of molecules of H_2 , N_2 , O_2 , and HBr is

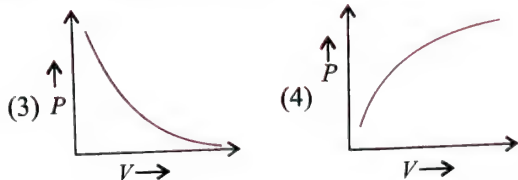
- (1) $\text{H}_2 > \text{N}_2 > \text{O}_2 > \text{HBr}$ (2) $\text{HBr} > \text{O}_2 > \text{N}_2 > \text{H}_2$
- (3) $\text{HBr} > \text{H}_2 > \text{O}_2 > \text{N}_2$ (4) $\text{N}_2 > \text{O}_2 > \text{H}_2 > \text{HBr}$

67. Which of the following statements is wrong for gases?

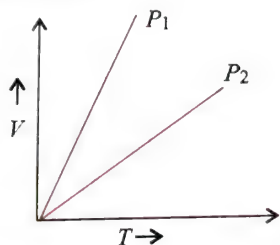
- (1) Gases do not have a definite shape and volume.
- (2) Volume of the gas is equal to volume of container confining the gas.
- (3) Confining gas exerts uniform pressure on the walls of container in all directions.
- (4) Mass of gas cannot be determined by weighing a container in which it is enclosed.

68. 3.2 g oxygen is diffused in 10 min. In similar conditions, 2.8 g nitrogen will diffuse in
 (1) 9.3 min (2) 8.2 min
 (3) 7.6 min (4) 11.8 min
69. At what temperature will the molar kinetic energy of 0.3 mol of 'He' be the same as that of 0.4 mol of argon at 400 K?
 (1) 700 K (2) 500 K (3) 800 K (4) 400 K
70. Which of the following statements is not correct about the three states of matter, i.e., solid, liquids and gas?
 (1) Molecules of a solid possess least energy whereas those of a gas possess highest energy.
 (2) The density of a solid is highest whereas that of gases is lowest.
 (3) Gases like liquids possess definite volumes.
 (4) Molecules of a solid possess vibratory motion.
71. Which of the following is true about gaseous state?
 (1) Thermal energy = Molecular attraction
 (2) Thermal energy \gg Molecular attraction
 (3) Thermal energy \ll Molecular attraction
 (4) Molecular forces \gg Those in liquids
72. Which of the following is not a correct postulate of kinetic theory of gases?
 (1) The molecules of a gas are continuously moving in different directions with different velocities.
 (2) The average kinetic energy of the gas molecules is directly proportional to the absolute temperature of the gas.
 (3) The volume of the gas is due to the large number of molecules present in it.
 (4) The pressure of the gas is due to the collision of the molecules on the walls of the container.
73. In the van der Waals equation
 (1) b is the volume occupied by the gas molecules
 (2) b is four times the volume occupied by the gas molecules
 (3) b is the correction factor for intermolecular attraction
 (4) None of these
74. According to kinetic theory of gases, for a diatomic molecule
 (1) The pressure exerted by the gas is proportional to the mean velocity of the molecules
 (2) The pressure exerted by the gas is proportional to the root mean square velocity of the molecules.
 (3) The root mean square velocity is inversely proportional to the temperature.
 (4) The mean transitional kinetic energy of the molecules is proportional to the absolute temperature.
75. A vessel is filled with a mixture of oxygen and nitrogen. At what ratio of partial pressures will the mass of gases be identical?
 (1) $P(\text{O}_2) = 0.785P(\text{N}_2)$ (2) $P(\text{O}_2) = 8.75P(\text{N}_2)$
 (3) $P(\text{O}_2) = 11.4P(\text{N}_2)$ (4) $P(\text{O}_2) = 0.875P(\text{N}_2)$
76. Select one correct statement. In the gas equation, $PV = nRT$
 (1) n is the number of molecules of a gas.
 (2) n moles of the gas have a volume V .
 (3) V denotes volume of one mole of the gas.
 (4) P is the pressure of the gas when only one mole of gas is present.
77. When is deviation more in the behaviour of a gas from the ideal gas equation $PV = nRT$?
 (1) At high temperature and low pressure
 (2) At low temperature and high pressure
 (3) At high temperature and high pressure
 (4) At low temperature and low pressure
78. An ideal gas obeying kinetic theory of gases can be liquefied, if
 (1) Its temperature is more than critical temperature T_c
 (2) Its pressure is more than critical pressure P_c
 (3) Its pressure is more than P_c at a temperature less than T_c
 (4) It cannot be liquefied at any value of P and T
79. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, KE of CO_2 and N_2 molecules at the same temperature?
 (1) $\text{KE}_{\text{CO}} = \text{KE}_{\text{N}_2}$ (2) $\text{KE}_{\text{CO}} > \text{KE}_{\text{N}_2}$
 (3) $\text{KE}_{\text{CO}} < \text{KE}_{\text{N}_2}$
 (4) Cannot be predicted unless volumes of the gases are given
80. Which expression gives average speed of gas molecules?
 (1) $\sqrt{\frac{8RT}{M}}$ (2) $\frac{3RT}{M}$
 (3) $\left[\frac{8RT}{\pi M}\right]^{1/2}$ (4) $\frac{8RT}{3.14M}$
81. Under similar conditions, which of the following gas will have same value of μ_{rms} as CO_2 ?
 (1) NO (2) C_3H_8 (3) CO (4) N_2
82. 15 L of gas at STP is subjected to four different conditions of temperature and pressure as shown below. In which case the volume will remain unaffected?
 (1) 273 K, 2 bar pressure
 (2) 273°C , 0.5 atm pressure
 (3) 546°C , 1.5 atm pressure
 (4) 273°C and 2 atm pressure
83. A gaseous mixture contains oxygen and nitrogen in the ratio of 1:8 by mass. The ratio of their respective number of molecules ($N_{\text{O}_2} : N_{\text{N}_2}$) is
 (1) 1:8 (2) 1:1 (3) 7:64 (4) 1:2
84. Among the plots of P vs V , as given below, which one corresponds to Boyle's law?





85. The pressure of a gas is due to
- (1) Rapid intermolecular collisions
 - (2) Molecular impacts against the walls of vessel
 - (3) Voids between the gas molecules
 - (4) Ideal behaviour of gases
86. V vs T curves at different pressures P_1 and P_2 for an ideal gas are shown below:



Which one of the following is correct?

- (1) $P_1 > P_2$ (2) $P_1 < P_2$ (3) $P_1 = P_2$ (4) $P_2/P_1 = 1/2$

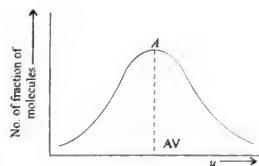
Multiple Correct Answers Type

1. Which of the following statements is/are correct?

- (1) The van der Waals constant a is a measure of attractive force.
- (2) The van der Waals constant b is also called co-volume or excluded volume.
- (3) b is expressed in L mol^{-1} .
- (4) b is one-third of critical volume.

2. Point A in the given curve shifts to higher value of velocity if

- (1) T is increased
- (2) P is decreased
- (3) V is decreased
- (4) Molecular weight M is decreased



3. Which of the following processes would lead to an increase in the average speed of the molecules of an ideal gas system?

- (1) Decreasing the temperature of the system
- (2) Compressing the gas with a piston
- (3) Expanding the gas into a vacuum
- (4) Heating the system keeping V and P constant.

4. According to the kinetic theory of gases

- (1) Pressure of a gas is due to collisions of molecules with each other
- (2) Kinetic energy is proportional to square root of the temperature
- (3) Pressure of a gas is due to collisions of molecules against the sides of the container
- (4) There is no force of attraction between gas molecules

5. For two gases A and B with molecular weights M_A and M_B , respectively, it is observed that at a certain temperature T , the mean velocity of A is equal to the V_{rms} of B . Thus, the mean velocity of A can be made equal to the mean velocity of B , if

- (1) A is at temperature T and B is at T' such that $T > T'$
- (2) Temperature of A is lowered to T_2 while B is at T such that $T_2 < T$
- (3) Both A and B are raised to a higher temperature
- (4) Heat energy supplied to A

6. Which of the following statements is/are true?

- (1) The ratio of the mean speed to the rms speed is independent of the temperature.
- (2) The square of the mean speed of the molecules is equal to the square of the rms speed at a certain temperature.
- (3) Mean kinetic energy of the gas molecules at any given temperature is independent of the mean speed.
- (4) The difference between the rms speed and the mean speed at any temperature for different gases diminishes as larger, and yet larger molar masses are considered.

7. If for two gases of molecular weights M_A and M_B at temperature T_A and T_B , respectively, $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases?

- (1) PV if mass of gases taken are same
- (2) Pressure
- (3) KE per mole
- (4) V_{rms}

8. Molecular attraction and size of the molecules in a gas are not negligible at

- (1) Critical point
- (2) High pressure
- (3) High temperature and low pressure
- (4) Low temperature and high pressure

9. If 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C , keeping the volume constant, its pressure would become

- (1) $1/273$ atm
- (2) 2 atm
- (3) $\frac{1}{2}$ atm
- (4) $5.05 \times 10^4 \text{ N m}^{-2}$

10. The compressibility factor of a gas is greater than unity at STP. Therefore

- (1) $V_m > 22.4 \text{ L}$
- (2) $V_m < 22.4 \text{ L}$
- (3) $V_m = 22.4 \text{ L}$
- (4) The gas will become less liquefiable

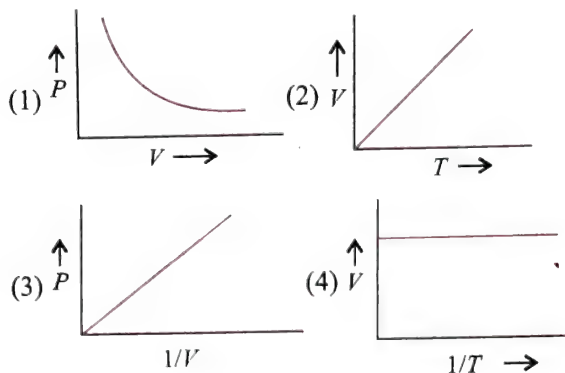
11. Select the correct statements.

- (1) Vapour may be condensed to liquid by the application of pressure.
- (2) To liquefy a gas one must lower the temperature below T_c and apply pressure.
- (3) At T_c , there is no distinction between liquid and vapour states.
- (4) At the T_c , density of liquid is very high as compared to its gaseous state.

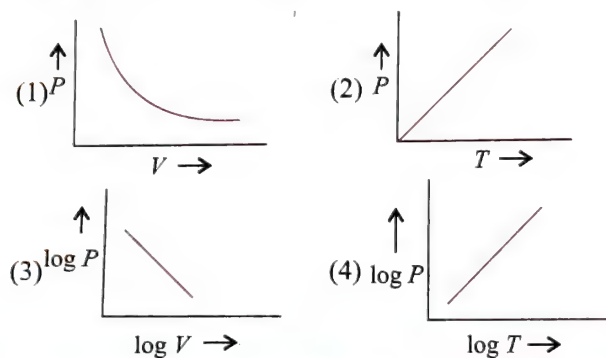
12. Which of the following statements is/are correct?
- All real gases are less compressible than ideal gases at high pressure.
 - Hydrogen and helium are more compressible than ideal gases for all values of pressure.
 - Except H_2 and He, the compressibility factor $Z \left(= \frac{PV}{nRT} \right) < 1$ for all gases at low pressure.
 - The compressibility factor of real gases is independent of temperature.
13. Precisely 1 mol of helium and 1 mol of neon are placed in a container. Indicate the correct statements about the system.
- Molecules of the two gases strike the wall of the container with same frequency.
 - Molecules of helium strike the wall more frequently.
 - Molecules of helium have greater average molecular speed.
 - Helium exerts larger pressure.
14. Which of the following statements is/are true?
- Hydrogen diffuses four times faster than oxygen.
 - The temperature of a real gas changes when it expands adiabatically in vacuum.
 - An ideal gas undergoes cooling effect when it suffers an adiabatic expansion in vacuum.
 - The Joule-Thomson coefficient $\left(\frac{dT}{dP} \right)_H$ of an ideal gas is zero.
15. The root mean square velocity of an ideal gas in a closed container of fixed volume is increased from $5 \times 10^4 \text{ cm s}^{-1}$ to $10 \times 10^4 \text{ cm s}^{-1}$. Which of the following statements correctly explains how the change is accomplished?
- By heating the gas, the temperature is doubled.
 - By heating the gas, the pressure is quadrupled.
 - By heating the gas, the temperature is quadrupled.
 - By heating the gas, the pressure is doubled.
16. In the equation $PV = RT$, the value of R will not depend upon
- The nature of the gas
 - The temperature of the gas
 - The pressure of the gas
 - Units of measurement
17. Which is the value of R ?
- $1.99 \text{ cal deg}^{-1} \text{ mol}^{-1}$
 - $0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$
 - $9.8 \text{ kcal deg}^{-1} \text{ mol}^{-1}$
 - $8.3 \text{ J deg}^{-1} \text{ mol}^{-1}$
18. Boyle's law may be expressed as
- $(dP/dV)_T = K/V$
 - $(dP/dV)_T = -K/V^2$
 - $(dP/dV)_T = -K/V$
 - $V \propto 1/P$
19. Which forces of attraction are responsible for liquefaction of H_2 ?
- Coulombic forces
 - Dipole forces

- Hydrogen bonding
 - van der Waals forces
20. According to Charles' law
- $(dV/dT)_P = K$
 - $(dV/dT)_P = -K$
 - $(dV/dT)_P = -K/T$
 - $V \propto T$
21. In van der Waals equation of gases, the kinetic equation for gas is modified with respect to
- Repulsive forces
 - Attractive forces between the gaseous molecules
 - Actual volume of the gas
 - Pressure of the molecules
22. Which of the following is/are correct about Charles' law?
- $(\partial V/\partial T)_P = \text{Constant}$
 - $V \propto T$ at constant P and n
 - $V \propto P$ at constant T, n
 - $V \propto T$ is constant at constant P, n
23. Which of the following gases is/are heavier than dry air?
- Moist air
 - Oxygen
 - Moist nitrogen
 - Hydrogen sulphide
24. One mole of which of the following will have 22.7 L at STP (1 bar, 273.15 K)?
- SO_2
 - He
 - H_2O
 - CCl_4
25. The gas constant has units
- $\text{L atm K}^{-1} \text{ mol}^{-1}$
 - $\text{L atm}^{-1} \text{ K}^{-1} \text{ mol}^{-1}$
 - $\text{atm cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$
 - erg K^{-1}
26. Which of the following pair of gases will have same rate of diffusion under similar conditions?
- H_2 and He
 - CO_2 and N_2O
 - CO and C_2H_4
 - NO and CO
27. Which of the following statements is/are correct about real gases?
- The molecules do cause attractive forces on each another.
 - They obey gas laws at low temperature and high pressure.
 - They show deviations from ideal behaviour.
 - The molecules have negligible mass.
28. At very high pressure, the van der Waals equation reduces to
- $PV = RT + Pb$
 - $PV = \frac{aRT}{V^2}$
 - $P = \frac{RT}{V - b}$
 - $PV = RT - \frac{a}{V}$
29. To which of the following mixtures Dalton's law is not applicable?
- CO_2 and CO at room temperature
 - Ammonia and hydrogen chloride at room temperature
 - NH_3 and steam at room temperature
 - He and H_2

30. Which of the following plots is/are correct?



31. Which of the following plots is/are correct?



Linked Comprehension Type

Paragraph 1

Two flasks A and B have equal volume. A is maintained at 300 K and B at 600 K. While A contains H_2 gas, B has an equal mass of CH_4 gas. Assuming ideal behaviours for both the gases, answer the following:

- Flask containing greater number of molecules
 (1) A (2) B
 (3) Both A and B (4) None
- Flask in which pressure is higher
 (1) A (2) B
 (3) Both A and B (4) None
- Flask in which the compressibility factor is greater
 (1) Flask A (2) Flask B
 (3) Both A and B (4) None
- Flask in which the total kinetic energy is greater
 (1) A (2) B
 (3) Both A and B (4) None
- Flask with greater molar kinetic energy
 (1) A (2) B
 (3) Both A and B (4) None
- Flask in which molecules are moving faster
 (1) A (2) B
 (3) Both A and B (4) None

Paragraph 2

The van der Waals constant for gases A , B , and C are as follows:

Gas	a ($\text{dm}^6 \text{ kPa mol}^{-2}$)	b ($\text{dm}^3 \text{ mol}^{-1}$)
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Answer the following:

- Which gas has the highest critical temperature?
 (1) A (2) B (3) C (4) None
- Which gas has the largest molecular volume?
 (1) A (2) B (3) C (4) None
- Which gas has the most ideal behaviour around STP?
 (1) A (2) B (3) C (4) None

Paragraph 3

For the given ideal gas equation $PV = nRT$, answer the following questions:

- In the above equation, the value of universal gas constant depends only upon
 (1) The nature of the gas
 (2) The pressure of the gas
 (3) The temperature of the gas
 (4) The units of measurement
- At constant temperature, in a given mass of an ideal gas
 (1) The ratio of pressure and volume always remains constant
 (2) Volume always remains constant
 (3) Pressure always remain constant
 (4) The product of pressure and volume always remains constant
- Which of the following does not represent ideal gas equation?
 (1) $PV = \frac{1}{3} mNv$ (2) $PV = nRT$
 (3) $P = \rho \frac{RT}{M}$ (4) $PV = RT$
- An ideal gas will have maximum density when
 (1) $P = 1 \text{ atm}$, $T = 300 \text{ K}$
 (2) $P = 2 \text{ atm}$, $T = 150 \text{ K}$
 (3) $P = 0.5 \text{ atm}$, $T = 600 \text{ K}$
 (4) $P = 1.0 \text{ atm}$, $T = 500 \text{ K}$
- Which of the following is incorrect according to the ideal gas equation?
 (1) $V \propto T$ (2) $P \propto \frac{1}{T}$ (3) $P \propto V$ (4) $V \propto n$

Paragraph 4

Using van der Waals equation $\left(P + \frac{a}{V^2}\right)(V - b) = RT$, answer the following questions:

- The van der Waals equation explains the behaviour of
 (1) Ideal gases (2) Real gases
 (3) Vapours (4) Non-real gases

16. The term that accounts for intermolecular forces in the van der Waals equation for non-ideal gas is

(1) RT (2) $V - b$

(3) $\left(P + \frac{a}{V^2}\right)$ (4) RT^{-1}

17. The term that accounts for effective volume in the van der Waals equation for non-ideal gas is

(1) RT (2) $V - b$

(3) $\left(P + \frac{a}{V^2}\right)$ (4) RT^{-1}

18. At high pressure, the van der Waals equation gets reduced to

(1) $\left(P + \frac{a}{V^2}\right)V = RT$

(2) $P(V - b) = RT$

(3) $PV = RT$

(4) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

Paragraph 5

Compressibility factor $Z = \frac{PV}{RT}$. Considering ideal gas, real gas,

and gases at critical state, answer the following questions:

19. The compressibility factor of an ideal gas is

(1) 0 (2) 1 (3) 2 (4) 3

20. The compressibility factor of a real gas is

(1) 0 (2) 1 (3) $\neq 1$ (4) None

21. The compressibility of a gas is less than unity at STP, therefore

(1) $V_m > 22.4 \text{ L}$ (2) $V_m < 22.4 \text{ L}$

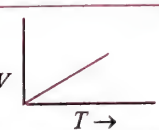
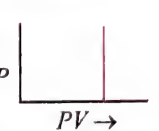

(3) $V_m = 22.4 \text{ L}$ (4) $V_m = 44.8 \text{ L}$

22. Z_c at T_c , P_c , and V_c is

(1) $3/8$ (2) $4/8$ (3) 1 (4) 0

Matrix Match Type

1. Match the items of columns I and II.

Column I	Column II
a. Boyle's law	p. 
b. Charles' law	q. 
c. Gay-Lussac's law	r. 

2. Match the items of columns I and II

Column I	Column II
a. Boyle's law	p. $V \propto T$
b. Charles' law	q. $P_{\text{total}} = P_A + P_B + \dots$
c. Gay-Lussac's law	r. $V \propto 1/P$
d. Dalton's law	s. $P \propto T$

3. Match the items of columns I and II.

Column I	Column II
a. Graham's law of diffusion	p. $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
b. Ideal gas law	q. $V \propto n$
c. Avogadro gas law	r. $PV = nRT$
d. van der Waals gas equation	s. $r \propto \sqrt{1/M}$

4. Match the items of columns I and II.

Column I	Column II
a. bar L mol^{-1}	p. Most probable speed
b. $(2RT/M)^{1/2}$	q. a/Rb
c. Boyle's temperature	r. $\propto P^{-1}$ at constant n and T
d. Mean free path	s. $\propto P^2$ at constant T
e. Collision frequency	t. Unit of ratio a/b

5. Match the items of columns I and II.

Column I	Column II
a. Co-volume	p. Molar volume of ideal gas
b. Compressibility factor	q. van der Waals constant b
c. Work done $\text{degree}^{-1} \text{ mol}^{-1}$	r. Depends on T and nature of liquid
d. 22.7 L at STP	s. PV/nRT
e. Vapour pressure of liquid	t. Universal gas constant

6. Match the items of columns I and II.

Column I	Column II
a. Critical temperature	p. Gas can be liquefied
b. Boyle's temperature	q. Deviate from ideal gas equation
c. Compressibility factor $(Z) < 1$	r. Gas follows the ideal gas equation
d. High temperature and low pressure	s. Assumption of no intermolecular force of attraction is valid

7. Match the items of columns I and II.

Column I	Column II
a. Diffusion of gas	p. High when molecular mass is low
b. Compressibility of gas ($Z < 1$)	q. $V_{\text{real}} < V_{\text{ideal}}$
c. V_{rms}	r. Increases with increase in temperature
d. Liquification of gas	s. Attractive force dominates

8. Match the items of columns I and II.

Column I	Column II
a. Z for ideal gas	p. $3/8$
b. Z for real gas at low P	q. $\left(1 + \frac{Pb}{RT}\right)$
c. Z for real gas at high P	r. 1
d. Z for critical state	s. $\left(1 - \frac{a}{RTV}\right)$
	t. $8/3$

9. Match the items of columns I and II

Column I	Column II
a. Attractive tendency dominate	p. $Z = 3/8$
b. At Boyle's temperature in the high pressure region	q. $Z < 1$
c. For a gas at very low pressure and at very high temperature	r. $Z > 1$
d. At the critical point	s. $Z = 1$

10. Match the items of column I and II.

Column I	Column II
a. Unit of van der Waals constant a	p. $\text{dyn cm}^{-2} \text{ s}$
b. Unit of van der Waals constant b	q. dyn cm^{-1}

c. Unit of R	r. $\text{J K}^{-1} \text{ mol}^{-1}$
d. Unit of surface tension (γ)	s. $\text{atm L}^2 \text{ mol}^{-2}$
e. Unit of coefficient of viscosity η	t. L mol^{-1}

Numerical Value Type

- The ratio of the inversion temperature of a gas to its Boyle temperature is
(1) 1 (2) 2 (3) 3 (4) 4
- A certain gas is at a temperature of 350 K. If the temperature is raised to 700 K, the average translational kinetic energy of the gas will increase by
(1) 2 (2) 3 (3) 4 (4) 5
- The value of compressibility factor (Z) for an ideal gas is
(1) 2 (2) 1 (3) 3 (4) 4
- The ratio of excluded volume (b) to molar volume of a gas molecule is
(1) 1 (2) 2 (3) 3 (4) 4
- What is the ratio of rate of diffusion of gas A and B. The molecular mass of A is 11 and molecular mass of B is 44.
(1) 1 (2) 2 (3) 3 (4) 4
- Initial volume of a gas is 1 L at temperature 100 K. What is the volume of a gas at 300 K.
(1) 1 (2) 2 (3) 3 (4) 4
- What is the average speed of a molecule, having a molecular mass of 529.5 g mol^{-1} . At temperature 100 K
(1) 1 (2) 2 (3) 3 (4) 4
- Calculate the moles of an ideal gas at pressure 2 atm and volume 1 L at a temperature of 97.5 K
(1) 1 (2) 2 (3) 3 (4) 4
- A 10 L box contains 41.4 g of a mixture of gases C_xH_x and C_xH_{12} . The total pressure at 44°C in flask is 1.56 atm. Analysis revealed that the gas mixture has 87% total C and 13% total H. Find out the value of x
(1) 1 (2) 3 (3) 5 (4) 2
- The rate of diffusion of methane is twice that of X. The molecular mass of X is divided by 32. What is value of x is?
(1) 1 (2) 2 (3) 3 (4) 4

Archives

JEE MAIN

Single Correct Answer Type

- If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, then how many moles of water are in the vapour phase when equilibrium is established?

(Given, vapor pressure of H_2O at 300 K is 3170 Pa; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

- (1) $5.56 \times 10^{-3} \text{ mol}$ (2) $1.53 \times 10^{-2} \text{ mol}$
(3) $4.46 \times 10^{-2} \text{ mol}$ (4) $1.27 \times 10^{-3} \text{ mol}$

(AIEEE 2010)

- a and b are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because
(1) a and b for $\text{Cl}_2 > a$ and b for C_2H_6
(2) a and b for $\text{Cl}_2 < a$ and b for C_2H_6
(3) a for $\text{Cl}_2 > a$ for C_2H_6 but b for $\text{Cl}_2 > b$ for C_2H_6
(4) a for $\text{Cl}_2 > a$ for C_2H_6 but b for $\text{Cl}_2 < b$ for C_2H_6
- The molecular velocity of any gas is
(1) Inversely proportional to the square root of temperature
(2) Inversely proportional to absolute temperature

(AIEEE 2011)

- (3) Directly proportional to square of temperature
 (4) Directly proportional to square root of temperature

(AIEEE 2011)

4. When r , p and M represent rate of diffusion, pressure and molecular mass, respectively, then the ratio of the rates of diffusion (r_A/r_B) of two gases A and B, is given as
 (1) $(p_A/p_B)^{1/2} (M_A/M_B)$ (2) $(p_A/p_B) (M_A/M_B)^{1/2}$
 (3) $(p_A/p_B)^{1/2} (M_B/M_A)$ (4) $(p_A/p_B) (M_B/M_A)^{1/2}$

(AIEEE 2011)

5. The compressibility factor for a real gas at high pressure is

(1) $1 + \frac{RT}{pb}$ (2) 1

(3) $1 + \frac{pb}{RT}$ (4) $1 - \frac{pb}{RT}$ (AIEEE 2012)

6. For gaseous state, if most probable speed is denoted by C^* , average speed by \bar{C} and means square speed by C , then for a large number of molecules, the ratios of these speeds are

(1) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$

(2) $C^* : \bar{C} : C = 1.128 : 1.225 : 1$

(3) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$

(4) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$ (JEE Main 2013)

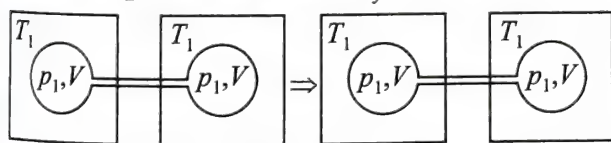
7. If Z is a compressibility factor, van der Waals' equation at low pressure can be written as

(1) $Z = 1 + \frac{RT}{pb}$ (2) $Z = 1 - \frac{a}{VRT}$

(3) $Z = 1 - \frac{pb}{RT}$ (4) $Z = 1 + \frac{pb}{RT}$

(JEE Main 2014)

8. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2 . The final pressure p_f is:



(1) $2p_i \left(\frac{T_1 T_2}{T_1 + T_2} \right)$ (2) $p_i \left(\frac{T_1 T_2}{T_1 + T_2} \right)$

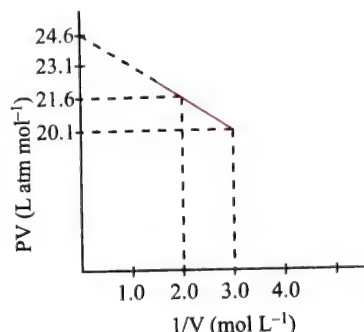
(3) $2p_i \left(\frac{T_1}{T_1 + T_2} \right)$ (4) $2p_i \left(\frac{T_2}{T_1 + T_2} \right)$

(JEE Main 2016)

(1) nb (2) $\frac{an^2}{V^2}$ (3) $-\frac{an^2}{V^2}$ (4) $-nb$

(IIT-JEE 2009)

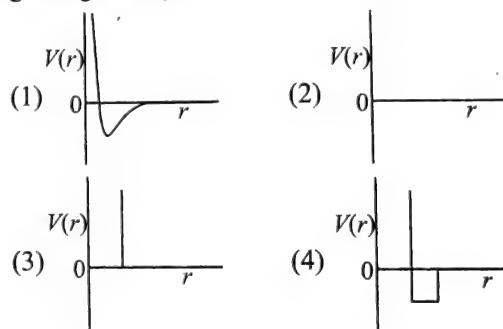
2. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the PV vs $1/V$ plot is shown below. The value of the van der Waals constant a ($\text{atm} \cdot \text{L}^2 \cdot \text{mol}^{-2}$) is



(1) 1.0 (2) 4.5 (3) 1.5 (4) 3.0

(IIT-JEE 2012)

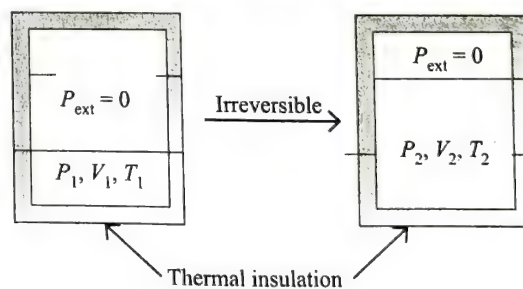
3. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for the gas is given by



(JEE Advanced 2015)

Multiple Correct Answers Type

1. An ideal gas in a thermally insulated vessel at internal pressure $= P_1$, volume $= V_1$ and absolute temperature $= T_1$ expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2 , V_2 and T_2 , respectively. For this expansion,



(1) $q = 0$ (2) $T_2 = T_1$
 (3) $P_2 V_2 = P_1 V_1$ (4) $P_2 V_2^\gamma = P_1 V_1^\gamma$

(JEE Advanced 2014)

2. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are)

JEE ADVANCED

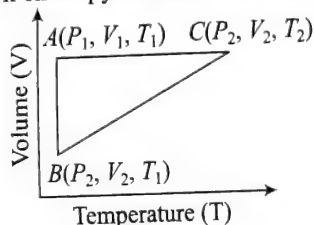
Single Correct Answer Type

1. The term that is correct for the attractive forces present in a real gas in the van der Waals equation is

- (1) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions
- (2) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$
- (3) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic
- (4) The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1

(JEE Advanced 2017)

3. A reversible cyclic process for an ideal gas is shown below. Here, P , V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q , w , H and U are heat, work enthalpy and internal energy, respectively.

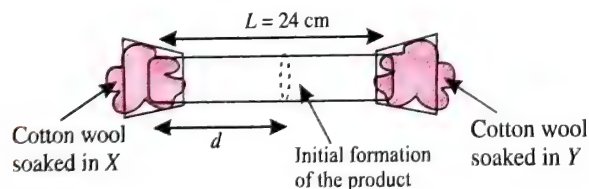


- (1) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$
- (2) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
- (3) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$
- (4) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

(JEE Advanced 2018)

Linked Comprehension Type

X and Y are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in X and the other soaked in Y , are simultaneously placed at the ends of a tube of length $L = 24 \text{ cm}$, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K . Vapours of X and Y react to form a product which is first observed at a distance $d \text{ cm}$ from the plug soaked in X . Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



1. The value of d in cm (shown in the figure), as estimated from Graham's law, is
(1) 8 (2) 12 (3) 16 (4) 20
2. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to
(1) larger mean free path for X as compared to that of Y .
(2) larger mean free path for Y as compared to that of X .
(3) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas.
(4) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas.

(JEE Advanced 2014)

Numerical Value Type

1. At 400 K , the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K . Calculate the molecular weight of the gas Y .

(IIT-JEE 2009)

2. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is

(JEE Advanced 2016)

3. A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across (Figure 2), the volume (m^3) of the compartment A after the system attains equilibrium is

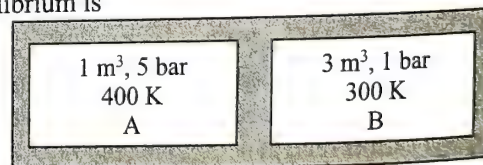


Figure 1

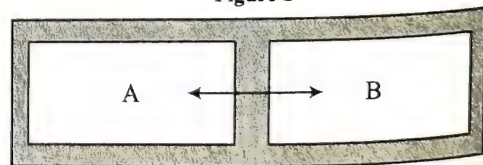


Figure 2

(JEE Advanced 2018)

EXERCISES

Single Correct Answer Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (1) | 2. (4) | 3. (2) | 4. (1) | 5. (1) |
| 6. (4) | 7. (1) | 8. (2) | 9. (3) | 10. (3) |
| 11. (3) | 12. (1) | 13. (2) | 14. (1) | 15. (3) |
| 16. (4) | 17. (2) | 18. (3) | 19. (1) | 20. (3) |
| 21. (4) | 22. (2) | 23. (3) | 24. (3) | 25. (4) |
| 26. (3) | 27. (1) | 28. (3) | 29. (4) | 30. (3) |
| 31. (1) | 32. (2) | 33. (2) | 34. (2) | 35. (3) |
| 36. (1) | 37. (4) | 38. (2) | 39. (1) | 40. (4) |
| 41. (1) | 42. (2) | 43. (4) | 44. (2) | 45. (1) |
| 46. (2) | 47. (4) | 48. (3) | 49. (1) | 50. (2) |
| 51. (2) | 52. (3) | 53. (3) | 54. (2) | 55. (1) |
| 56. (3) | 57. (1) | 58. (1) | 59. (1) | 60. (3) |
| 61. (1) | 62. (3) | 63. (1) | 64. (3) | 65. (4) |
| 66. (1) | 67. (4) | 68. (1) | 69. (4) | 70. (3) |
| 71. (2) | 72. (3) | 73. (2) | 74. (4) | 75. (4) |
| 76. (2) | 77. (2) | 78. (4) | 79. (1) | 80. (3) |
| 81. (2) | 82. (4) | 83. (3) | 84. (3) | 85. (2) |
| 86. (2) | | | | |

Multiple Correct Answers Type

- | | | |
|------------------|---------------|---------------|
| 1. (1, 2, 3, 4) | 2. (1, 4) | 3. (2, 4) |
| 4. (3, 4) | 5. (1, 4) | 6. (1, 3, 4) |
| 7. (1, 4) | 8. (1, 2, 4) | 9. (3, 4) |
| 10. (1, 4) | 11. (1, 2, 3) | 12. (1, 3) |
| 13. (2, 3) | 14. (1, 4) | 15. (2, 3) |
| 16. (1, 2, 3) | 17. (1, 2, 4) | 18. (2, 4) |
| 19. (2, 4) | 20. (1, 4) | 21. (3, 4) |
| 22. (1, 2) | 23. (2, 4) | 24. (1) |
| 25. (2, 3) | 26. (2, 3) | 27. (1, 3) |
| 28. (1, 3) | 29. (2, 3) | 30. (1, 2, 3) |
| 31. (1, 2, 3, 4) | | |

Linked Comprehension Type

- | | | | |
|---------|---------|---------|---------|
| 1. (1) | 2. (1) | 3. (3) | 4. (1) |
| 5. (2) | 6. (1) | 7. (2) | 8. (3) |
| 9. (1) | 10. (4) | 11. (4) | 12. (1) |
| 13. (2) | 14. (3) | 15. (2) | 16. (3) |
| 17. (2) | 18. (1) | 19. (2) | 20. (4) |
| 21. (2) | 22. (1) | | |

Matrix Match Type

Q.No.	a	b	c	d	e
1.	q	p	r	—	—
2.	r	p	s	q	—
3.	s	r	q	P	—
4.	t	p	q	r	s
5.	q	s	t	p	r
6.	p	r	q	s	—
7.	p	q	r	s	—
8.	r	s	q	p	—
9.	q	r	s	p	—
10.	s	t	r	q	p

Numerical Value Type

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (2) | 2. (1) | 3. (2) | 4. (4) | 5. (2) |
| 6. (3) | 7. (2) | 8. (4) | 9. (3) | 10. (2) |

ARCHIVES

JEE Main

Single Correct Answer Type

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (4) | 2. (4) | 3. (4) | 4. (2) | 5. (3) |
| 6. (3) | 7. (2) | 8. (4) | | |

JEE Advanced

Single Correct Answer Type

- | | | |
|--------|--------|--------|
| 1. (2) | 2. (3) | 3. (3) |
|--------|--------|--------|

Multiple Correct Answers Type

- | | | |
|--------------|--------------|-----------|
| 1. (1, 2, 3) | 2. (1, 3, 4) | 3. (2, 3) |
|--------------|--------------|-----------|

Linked Comprehension Type

- | | |
|--------|--------|
| 1. (3) | 2. (4) |
|--------|--------|

Numerical Value Type

- | | | |
|--------|--------|-----------|
| 1. (4) | 2. (4) | 3. (2.22) |
|--------|--------|-----------|

6

Thermodynamics

OVERVIEW

1. **Thermodynamics:** It is a branch of science which deals with the interconversion of various forms of energies. It also governs transformation of heat into work and vice-versa.
2. Chemical thermodynamics is the branch of thermodynamics which deals with the study of processes involving chemical energy only.
3. **Importance of thermodynamics**
 - i. To predict the feasibility of a process.
 - ii. To predict the yield of the products.
 - iii. To deduce important generalisation and their mathematical expressions like distribution law, phase rule, etc.
4. **Limitations of thermodynamics**
 - i. It deals with macroscopic quantities and not with microscopic quantities.
 - ii. It predicts feasibility but does not tell about the rate of reaction.
 - iii. It concerns only with initial and final states and does not deal with path by which the change is brought about.
5. **System.** It is a part of the universe which is selected for thermodynamics investigation.
6. **Surroundings.** The part of the universe other than the system is called surroundings. The system and surroundings are separated by a real or imaginary boundary.
7. **Types of systems.** On the basis of the composition, the system may be:
 - a. **Homogeneous system.** A system having uniform nature throughout and consists of one phase only.
 - b. **Heterogeneous system.** A system which is not uniform throughout and consists of more than one phase.
- c. **On the basis of exchange of mass and energy, the system may be:**
 - i. **Open system.** The system which can exchange mass as well as energy with the surroundings. For example, tea in a cup or a solution of CuSO_4 in a beaker.
 - ii. **Closed system.** The system which can exchange energy with the surroundings but not mass. For example, heating of solid iodine in a sealed container. Here the solid iodine sublimes to iodine vapours, but iodine vapours cannot escape from the container.
 - iii. **Isolated system,** The system which can neither exchange energy nor mass with the surroundings. Such a system is sealed and insulated. For example, piece of ice in a thermos flask.
8. **State of system.** The conditions of existence of a system when its macroscopic properties have definite values is called state of the system.
9. **State functions.** State function is a quantity or property, the change in the value of which depends only on the initial and final states of the system and is independent of path.
10. **Thermodynamic properties**
 - a. **Extensive properties.** The properties of the system which depend upon the amount of substance in the system. For example, mass, volume, energy, enthalpy work, etc.
 - b. **Intensive properties.** The properties of the system which do not depend upon the amount of substance present. For example, temperature, pressure, viscosity, surface tension, density, refractive index, specific heat, etc.
11. **Thermodynamic process**
 - a. **Isothermal process.** It is one in which temperature of the system remains constant ($\Delta T = 0$)
 - b. **Isobaric process.** It is one in which the pressure of the system remains constant ($\Delta P = 0$)
 - c. **Isochoric process.** It is one in which the volume of the system remains constant ($\Delta V = 0$)
 - d. **Adiabatic process.** It is one in which the system does not exchange heat with the surroundings i.e., no heat enters or leaves the system ($\Delta q = 0$)
 - e. **Reversible process** The process which is carried out infinitesimally slowly so that all the changes occurring in the forward direction can be exactly reversed and the system maintains equilibrium with the surrounding at every stage of the process. It is a multistage process. For a process to be reversible, friction, resistance, etc., should be absent and secondly there should be thermodynamic equilibrium. It is an ideal process and cannot be observed in reality.
 - f. **Irreversible process** The process which is not carried out infinitesimally slowly so that all the changes

occurring in the forward direction cannot be exactly reversed and the system does not maintain equilibrium with the surrounding. It is a single stage process. All natural processes are irreversible in nature.

- g. **Cyclic process** It is the one in which the system returns to its original state after a number of reactions. For such a process $\Delta U = 0$ and $\Delta H = 0$.

12. Work and heat

- a. Work is a mode of energy transfer to or from a system with reference to the surroundings. When the system is in equilibrium no work is being done. It appears only during a change of state of the system.

Mathematically, mechanical work is given by the expression,

$$W_{\text{irr}} \geq -P_{\text{ext}} \Delta V$$

The differential form of expression is

$$dW = -P_{\text{ext}} dV$$

Maximum work is possible if P_{ext} is maximum. This is possible when the process is reversible. Thus,

$$W_{\text{rev}} \geq W_{\text{irr}}$$

Work done in isothermal reversible expansion of an ideal gas is given by

$$W_{\text{rev}} = -2.303 nRT \log \frac{V_2}{V_1} = -2.303 nRT \log \frac{P_1}{P_2}$$

- b. **Units of work.** C.G.S. unit of work is erg or dyne-cm
S.I. (or M.K.S.) unit of work is joule or N-m.

$$1 \text{ J} = 10^7 \text{ erg}$$

$$1 \text{ kJ} = 1000 \text{ J}$$

- c. **Heat, (q).** It may be defined as the amount of energy that flows between system and surroundings due to difference in temperature.

$$q = m \times c \times t$$

where m = mass of the substance, c = specific heat, t = temperature difference.

- d. **Units of heat** are calorie and joule

$$1 \text{ J} = 0.2390 \text{ cal}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ L-atm} = 101.3 \text{ J} = 24.206 \text{ cal} = 1.013 \times 10^9 \text{ ergs}$$

13. Conversion of heat into work (Carnot cycle)

The machine used for the conversion of heat into work is called heat engine. Carnot gave an imaginary reversible cycle which demonstrates the maximum conversion of heat into work. Here the system consists of one mole of an ideal gas enclosed in cylinder fitted with a frictionless piston. The heat engine takes heat from the reservoir at high temperature (called the **source**) converts some heat into work and returns the remaining heat to another reservoir at low temperature (called the **sink**). Steam engine is one common example.

- a. **Efficiency of heat engine.**

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

where W is the work done, Q_2 and Q_1 are the heat absorbed from the source and heat returned back to the sink respectively, T_2 and T_1 are the temperatures of the source and sink respectively. Larger the temperature difference between the source and sink, larger will be the efficiency of the engine.

Since T_1 has a finite positive value and is never zero, it is evident that η is always less than one.

$$\text{Also, } W = Q \left(\frac{T_2 - T_1}{T_2} \right)$$

14. Internal energy (U or E)

- a. It is the definite quantity of energy possessed by a substance and depends upon the chemical nature, temperature pressure and volume. It is a state function whose absolute value cannot be determined as it is a sum of many types of energies such as translation, rotational, vibrational, electronic, and bonding energy of molecules (coulombic energy) between the electrons and the nuclei in the atoms etc. and absolute value of each type cannot be determined.

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{bonding}} + U_{\text{electronic}}$$

However, the change in internal energy, ΔU can be calculated and is represented by

$$\Delta U = U_2 - U_1$$

ΔU also represent the heat change occurring during the process at constant volume and constant temperature (q_v). It is determined with the help of Bomb calorimeter

- b. **Sign convention of work (W)**

Old convention	New SI convention
Formula used: $q = \Delta U + W$	Formula used: $Q = \Delta U - W$
Work done by the system: +ve	Work done by the system: -ve
Work done on the system: -ve	Work done on the system: +ve

15. First law of thermodynamics

It states that energy can neither be created nor be destroyed although it can be converted from one form to another. This means that the total energy of the universe remains constant. This law was put forward by *Mayer and Helmholtz*.

Mathematical formulation:

$$q = \Delta U - W$$

where ΔU = internal energy change, q = heat change. W = work (it refers to all types of work, i.e., $W_{\text{expansion}}$ as well as $W_{\text{non-expansion}}$).

There are many indirect proofs in favour of first law.

For example,

- a perpetual motion machine cannot be constructed.
- energy is conserved during chemical reactions, and
- for every 4.184 J of work done, 1 calorie of heat is evolved.

16. Enthalpy or heat content (H)

Since majority of reactions are carried in open vessels therefore these are subjected to constant pressure conditions.

Since heat changes under such conditions are different from heat changes at constant volume conditions, therefore a new thermodynamic function, enthalpy denoted by H , is defined. It is mathematically expressed as

$$H = U + PV$$

Enthalpy is a state function and is an extensive property. The absolute value of H cannot be calculated but the change in enthalpy ΔH can be calculated. It represents heat change at constant pressure.

17. For **exothermic reactions**, $\Delta H < 0$, while for **endothermic reactions**, $\Delta H > 0$

- a. Exothermic reactions are chemical reactions which proceed with evolution of heat. In other words, heat is given out by the reacting substances and enthalpy of the products is lowered.

$$\begin{aligned} \text{or } H_p &< H_R \\ \Delta H &= H_p - H_R = -ve \end{aligned}$$

Hence ΔH is negative for exothermic reactions. Likewise ΔU is also negative in these reactions.

- b. Endothermic reactions are chemical reactions which proceed with absorption of heat by the reacting substances. The enthalpy of the products, therefore, becomes more than the enthalpy of reactants.

$$\begin{aligned} \text{or } H_p &> H_R \\ \Delta H &= H_p - H_R = +ve \end{aligned}$$

Hence, ΔH is +ve for endothermic reactions. Likewise ΔU is positive for these reactions.

18. Bond energy and bond dissociation energy

Bond dissociation energy is the energy required to break one mole of a particular type of bonds in gaseous molecules. Its unit is kJ mol^{-1} . It should be noted that

- In diatomic molecules, the terms bond energy and bond dissociation energy have same meaning, e.g., for H_2 molecules, the value is 433 kJ mol^{-1}
- In polyatomic molecules containing more than one similar bonds, the bond energy is average of bond dissociation energies of various similar bonds.

Use of bond energy data: To calculate enthalpy changes in a reaction.

$$\Delta H^\ominus = \Sigma \text{Bond energies of reactants} - \Sigma \text{Bond energies of products.}$$

19. Heat capacity

It is the heat required to raise the temperature of the system by one degree. For one mole of a pure substance, it is called **molar heat capacity (C_m)**.

Types of heat capacity

i. Heat capacity at constant volume, $C_V = \left[\frac{\partial E}{\partial T} \right]_V$

ii. Heat capacity at constant pressure, $C_P = \left[\frac{\partial H}{\partial T} \right]_P$

For an ideal gas, $C_P - C_V = R$

where R is gas constant. Thus, $C_P > C_V$

20. Heat of reaction

The heat change taking place during the reaction when the number of moles of reactants and products are the same as indicated by the balanced chemical equation, is referred to as **heat of reaction**. Thus heat of reaction is the quantity of heat evolved or absorbed in a reaction. It is denoted by ΔH and is expressed in **joules (J) or kilo joules (kJ)**.

$$\Delta H = \Sigma H_{(P)} - \Sigma H_{(R)}$$

For exothermic reactions: $\Sigma H_p < \Sigma H_R \quad \therefore \Delta H \text{ is } -ve$

For endothermic reactions: $\Sigma H_p > \Sigma H_R \quad \therefore \Delta H \text{ is } +ve$

21. Various forms of heats of reactions

Standard heat of formation is the heat of formation of the compound under standard conditions, 298 K and 1 atmosphere pressure are taken as standard conditions. *Standard heat of formation of all elements is taken as zero. If an element exists in more than one allotropic forms, the most stable allotropic form is taken as standard form.* Standard enthalpies of formation of graphite and rhombic sulphur are taken as zero.

Standard enthalpy of formation data can be used to calculate enthalpy of reaction.

$$\Delta H^\ominus_{\text{Reaction}} = \Sigma H^\ominus_f (\text{Products}) - \Delta H^\ominus_f (\text{Reactants})$$

22. Different type of standard enthalpy changes (based on IUPAC recommendations)

Transition enthalpy	Example	Definition	Symbol
1. Enthalpy of formation It is always negative	$\text{Na(s)} + 1/2\text{Cl}_2(\text{g}) \longrightarrow \text{NaCl(s)}$	One mole of the compound formed from its constituent elements.	$\Delta_f H^\ominus$
2. Enthalpy of combustion	$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(l)}$	One mole of the compound (fuel) is burnt completely in oxygen (oxidation).	$\Delta_{\text{comb}} H^\ominus$
3. Enthalpy of vaporisation	$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(g)}$	One mole of the vapour formed from the liquid without a change in temperature.	$\Delta_{\text{vap}} H^\ominus$
4. Enthalpy of fusion	$\text{H}_2\text{O(s)} \longrightarrow \text{H}_2\text{O(l)}$	One mole of the liquid formed from the solid without a change in temperature.	$\Delta_{\text{fus}} H^\ominus$
5. Enthalpy of atomisation	$\text{H}_2(\text{g}) \longrightarrow 2\text{H(g)}$	One mole of the gaseous substance broken into isolated atoms in the gaseous phase.	$\Delta_{\text{atom}} H^\ominus$

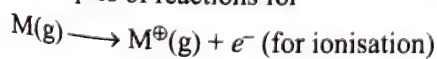
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6.	Enthalpy of reaction	$A \longrightarrow B$	Enthalpy change taking place in a reaction.	$\Delta_r H^\ominus$
7.	Enthalpy of neutralisation	$HCl(aq) + NaOH(aq) \longrightarrow H_2O + NaCl(aq)$	Enthalpy released when 1 g equivalent of an acid or (base) is completely neutralised by a base (or acid). Heat of neutralisation of strong acid-strong base = $-57.1 \text{ kJ} = -13.7 \text{ kcal}$	$\Delta_n H^\ominus$
8.	Enthalpy of sublimation	$H_2O(s) \longrightarrow H_2O(g)$	One mole of the vapour formed from the solid.	$\Delta_{\text{sub}} H^\ominus$
9.	Enthalpy of ionisation	$Na(g) \longrightarrow Na^+(g) + e^-$	One mole atoms ionised—all species in gaseous phase.	$\Delta_{\text{ion}} H^\ominus$
10.	Electron-gain enthalpy	$X(g) + e^- \longrightarrow X(g)$	One mole of anions being formed from all species in the gaseous phase.	$\Delta_{\text{eg}} H^\ominus$
11.	Bond dissociation enthalpy (bond A—B)	$HX(g) \longrightarrow H(g) + Cl(g)$	One mole of bonds broken—all species in the gaseous phase.	ΔH^\ominus_{A-B}
12.	Lattice enthalpy	$KCl(s) \longrightarrow K^+(g) + Cl^-(g)$ OR $K^+(g) + Cl^-(g) \longrightarrow KCl(s)$	Enthalpy released when the crystal lattice of one mole of a compound is formed from its constituent gaseous ions.	$\Delta_c H^\ominus$
13.	Enthalpy of solution or Enthalpy of dissolution	$A(s) + H_2O(\text{excess}) \longrightarrow A(aq)$	One mole of the solute dissolved in excess of solvent so that further dilution produces no enthalpy change.	$\Delta_{\text{sol}} H^\ominus$
14.	Enthalpy of hydration	a. $X^\pm(g) \longrightarrow X^\pm(aq)$ b. $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s)$	a. One mole of the ion in gaseous phase is hydrated to give hydrated ions. b. Enthalpy change occurring when one mole of anhydrous substance is dissolved in exact amount of water to give hydrated compound.	$\Delta_{\text{hyd}} H^\ominus$
15.	Enthalpy of mixing	Pure substances \longrightarrow Mixture	One mole of each of the two or more.	$\Delta_{\text{mix}} H^\ominus$
16.	Integral heat of solution	$KCl(s) + 200 H_2O(l)$ \downarrow $KCl(200 H_2O), \Delta H = +18.6 \text{ kJ}$	Enthalpy change of 1 mole of solute when it is dissolved in a pure solvent to give a solution of given concentration.	No symbol
17.	Differential heat of solution	Note: Integral and differential heat of solutions are not the same	Enthalpy change of 1 mole of solute when it is dissolved in such a large volume of solution of known concentration so that no enthalpy change occurs on further dilution.	No symbol
18.	Heat of hydrogenation	$CH_2 = CH_2(g) + H_2(g)$ \downarrow $CH_3 - CH_3(g)$	Enthalpy change when 1 mole of an unsaturated organic compound is fully hydrogenated.	No symbol
19.	Heat of transition	$S_{(r)} \rightarrow S_{(m)}$ $\Delta H = +2.5 \text{ kJ}$	Enthalpy change when 1 mole of the substance undergoes transition from one allotropic form to another.	No symbol

23. Ionisation energy and electron affinity

Ionisation energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for



$M(g) + e^- \longrightarrow M^-(g)$ (for electron gain)
at temperature T is

$$\Delta_r H^\ominus(T) = \Delta_r H^\ominus(0) + \int_0^T \Delta_r C_p^\ominus dT$$

The value of C_p for each species in the above reaction is

$$\frac{5R}{2} \left(C_V = \frac{3}{2} R \right)$$

So,

$$\Delta_r C_p^\ominus = +\frac{5}{2} R \text{ (for ionisation)}$$

$$\Delta_r C_p^\ominus = -\frac{5}{2} R \text{ (for electron gain)}$$

Therefore,

$$\Delta_r H^\ominus \text{ (ionisation enthalpy)}$$

$$= E_0 \text{ (ionisation energy)} + \frac{5}{2} RT$$

$$\Delta_r H^\ominus \text{ (electron gain enthalpy)}$$

$$= -EA \text{ (electron affinity)} - \frac{5}{2} RT$$

24. Laws of thermochemistry

- Laplace and Lavoisier law.** According to this law, heat absorbed or evolved in a chemical reaction is opposite and equal to heat change when the reaction is reversed.
- Hess's law of constant heat summation.** The heat of reaction depends only on the enthalpy of reactants and products and not at all on the intermediate products. In other words, ΔH for a reaction is independent of the path of manner by which the reaction is brought about.

Applications of Hess's law

- To determine heat of transition i.e., conversion of one allotropic modification to another.
- To determine heat of intermediate steps in a reaction.
- To calculate heat of reactions of known/unknown reactions.
- To calculate bond energies.

25. Zeroth Law of thermodynamics

According to this law, if two systems A and B separately are in thermal equilibrium with another system C, then system A and B will also be in thermal equilibrium with each other.

26. Second law of thermodynamics

The first law of thermodynamics does not help us to predict whether the process in question can occur spontaneously or not (i.e., whether it is feasible or not) and if so, in which direction. The answer to this problem is provided by second law of thermodynamics. The statement of the law is developed in terms of the entropy criterion.

The second law states that entropy of isolated system tends to increase and reaches a maximum value. This means that the most stable state of an isolated system is the state of maximum entropy.

There are several other statements of the second law.

- Clausius stated that it is impossible to transfer heat from a cold to hot reservoir without doing some work.
- Kelvin stated that it is impossible to convert all the heat taken from source to work, without losing some of it to colder reservoir.
- Caratheodory postulated that in the neighbourhood of every equilibrium state of a closed system, there are states which cannot be reached.

- Boltzmann stated that, nature tends to pass from a less probable to a more probable condition. The condition of maximum probability is the one of the maximum randomness.

27. Entropy

It is the extensive thermodynamic property of the system which provides a measure of its degree of disorder or randomness. It is denoted by S. The change in entropy during the process is mathematically given by the ratio of heat absorbed by the system (q) in the reversible manner to the temperature (T) at which it is absorbed.

$$\Delta S = (S_2 - S_1) = \frac{q_{\text{rev}}}{T}$$

It is a state function. The unit of entropy is $\text{J K}^{-1} \text{ mol}^{-1}$.

28. Spontaneous and non-spontaneous processes

- Spontaneous process.** The physical or chemical process which occurs in a particular set of conditions either of its own or after proper initiation is known as **spontaneous process**. All natural processes are spontaneous processes. Further, spontaneous process cannot reverse of their own. For a process to be spontaneous in isolated systems the sign of ΔS should be positive. Since large number of processes are carried out in open vessels therefore in such cases we have to take into account the total entropy change i.e., entropy change of system and entropy change of surrounding

$$\Delta S_{\text{total}} = \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} > 0$$

if system changes from A to B, either reversibly or irreversibly, then entropy change is given as

$$\Delta S_{\text{sys.}} = \frac{q_{\text{rev}}}{T}$$

and the corresponding entropy change in the surrounding

$$\Delta S_{\text{surr.}} = -\frac{q_{\text{rev}}}{T}$$

$$\text{i.e. } \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} = 0 \text{ (For reversible process)}$$

$$\text{or } \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} > 0 \text{ (For irreversible process)}$$

From the above expression follows the statement of **second law** that the *entropy of the universe (system and surroundings taken together) always increase during the course of any spontaneous change.*

b. Change in entropy (ΔS) and spontaneity of exothermic and endothermic process

- For an exothermic process, ΔS (surrounding) is always +ve.
 - If ΔS (system) is also positive, the process is always spontaneous as

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$
 - If ΔS (system) is negative, the process will be spontaneous only if ΔS_{Total} is positive. In such a case, the process will be spontaneous only if increase in entropy of the surrounding is more than the decrease in entropy of the system.

2. For an endothermic process, ΔS (surrounding) is always -ve. The process will be spontaneous only if the entropy of the system increases and the increase in entropy of the system should be more than the decrease in entropy of the surrounding such that $\Delta S_{\text{Total}} > 0$

c. **Non-spontaneous process.** A process that does not occur of its own, i.e., a process which does not have any natural tendency to occur is termed as **non-spontaneous process**.

To perform a non-spontaneous process, energy from some external source has to be supplied to the system. For example, lifting of water to higher level with the help of electric motor is a non-spontaneous process.

29. Entropy changes in processes

a. **Entropy change during isothermal reversible expansion of an ideal gas**

$$\Delta S = \frac{q_{\text{rev.}}}{T}$$

According to first law, $\Delta U = q + W$. As the process is isothermal, therefore, $\Delta U = 0$.

or $q = -W_{\text{rev.}}$

As $W_{\text{rev.}} = -nRT \ln \frac{V_2}{V_1} = 2.303 nRT \log \frac{V_2}{V_1}$

$\therefore q = 2.303 RT \log \frac{V_2}{V_1} = 2.303 RT \log \frac{P_1}{P_2}$

For 1 mole of a gas at constant temperature conditions, the entropy change is given as ($n = 1$)

$$\begin{aligned} \Delta S = \frac{q}{T} &= 2.303 \frac{RT}{T} \log \frac{V_2}{V_1} = 2.303 R \log \frac{V_2}{V_1} \\ &= 2.303 R \log \frac{P_1}{P_2} \end{aligned}$$

b. **Entropy change during adiabatic reversible expansion**

In such processes $q = 0$ at all stages hence $\Delta S = 0$. Thus, reversible adiabatic processes are called **isoentropic processes**.

c. **Entropy change when pressure is constant (isobaric process)**

$$\Delta S = 2.303 C_p \log \frac{T_1}{T_2}; C_p = \text{heat capacity at constant pressure.}$$

d. **Entropy change when volume is kept constant (isochoric process)**

$$\Delta S = 2.303 C_v \log \frac{T_2}{T_1}$$

e. Entropy change during phase transition

$$\Delta S = S_2 - S_1 = \frac{q_{\text{rev.}}}{T} = \frac{\Delta H}{T}$$

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}, \quad \Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T_{\text{vap.}}}$$

(fus. = Fusion, vap. = vaporisation)

30. a. Criterion of spontaneity

$$(dS)_{U, V} \geq 0 \quad (dG)_{T, P} \leq 0 \quad \text{or}$$

$$(dU)_{S, V} \leq 0 \quad \text{or} \quad (dH)_{S, P} \leq 0$$

where inequality ($<$ or $>$) refers to an irreversible process (spontaneous) while equality ($=$) refers to a reversible process at equilibrium.

b. **Exoergonic reactions.** An exoergonic reaction is a reaction which is accompanied by decrease of Gibbs energy i.e., a reaction for which the ΔG is negative. All spontaneous processes are exoergonic reactions.

c. **Endoergonic reactions.** An endoergonic reaction is a reaction which is accompanied by increase in Gibbs energy i.e., for which ΔG is positive. All non-spontaneous processes are endoergonic reactions.

d. **Effect of temperature on spontaneity**

i. For exothermic reaction, $\Delta H = -ve$

$$T\Delta S = +ve \text{ or } -ve$$

If $T\Delta S$ is $+ve$ then ΔH is always $-ve$

If $T\Delta S$ is $-ve$ then for ΔG to be $-ve$, T should be low. Thus, exothermic reactions are favoured by decrease in temperature.

ii. For endothermic reactions, $\Delta H = +ve$

$$T\Delta S = +ve \text{ or } -ve$$

If $T\Delta S$ is $-ve$, then $\Delta G > 0$ (reaction is non-spontaneous)

If $T\Delta S$ is $+ve$, then for ΔG to be $-ve$ T should be high. Thus, endothermic reactions are favoured by increase in temperature.

31. Gibbs's energy (G)

Gibb's energy of a system is the thermodynamic quantity, the decrease in the value of which during the process is equal to the useful work done by the system

$$(-\Delta G = -W_{\text{useful}}).$$

It is the amount of energy freely available from a system at particular conditions which can be put into useful work. During any process the change in Gibbs's energy is given by the expression

$$\Delta G = G_2 - G_1$$

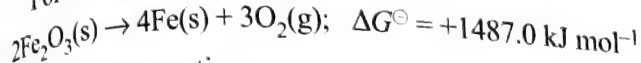
ΔG is also related to ΔH and ΔS as: $\Delta G = \Delta H - T\Delta S$

This expression is called **Gibb's Helmholtz equation**.

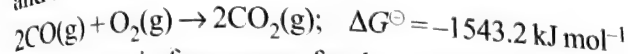
S. No.	Sign of ΔH	Sign of ΔS	$\Delta G = \Delta H - T\Delta S$	Remarks
1.	Negative	Positive	Always negative.	Spontaneous at all temperatures.
2.	Positive	Negative	Always positive.	Non-spontaneous at all temperatures.
3.	Positive	Positive	Positive at low temperature.	Non-spontaneous at low temperature.
			Negative at high temperature.	Spontaneous at high temperature.
4.	Negative	Negative	Negative at low temperature.	Spontaneous at low temperature.
			Positive at high temperature.	Non-spontaneous at high temperature.

a. Coupled reactions. A non-spontaneous reaction can be made spontaneous by coupling. When a non-spontaneous reaction (i.e., a reaction for which ΔG is positive) is coupled with another reaction for which ΔG is highly negative, then both the reactions can occur simultaneously.

For example, for the reaction



and for the reaction



The change in free energy for the combination of these two reactions,

$$\Delta G^\ominus = -56.2 \text{ kJ mol}^{-1}$$

is negative, the reduction of Fe_2O_3 with CO is spontaneous process.

b. Change in Gibbs's energy and equilibrium constant.

For a reversible reaction at constant temperature and constant pressure, the equilibrium composition of reaction mixture corresponds to lowest point on Gibbs's energy and progress of reaction curve.

i. $\Delta G^\ominus = -2.303RT \log k$.

ii. For endothermic reaction, $\Delta H^\ominus = +ve$,

$\therefore \ln k$ and hence k is small.

iii. For exothermic reaction, $\Delta H^\ominus = -ve$

$\therefore \ln k$ and hence k is large.

c. Change in Gibbs's energy and EMF of a cell

i. $\Delta G = W_{\text{max}}$,

For electrochemical cell, $\Delta G = -nF E_{\text{cell}}$.

ii. If reactants and products are in their standard state,

$$\Delta G^\ominus = -nF E_{\text{cell}}^\ominus$$

where n is the number of moles of electrons involved in the redox reaction and E_{cell} is the EMF of the cell.

33. Third law of thermodynamics

The entropy of a substance at absolute zero is taken to be zero. It is used in calculating absolute entropies of pure substances at different temperature.

$$S_T - S_0 = \Delta S = \int_0^T \frac{C_p dT}{T} = C_p \ln T = 2.303 C_p \log T$$

where S_T and S_0 are the entropies at T K and 0 K, respectively.

SOME IMPORTANT FORMULAE

1. Joule's relationship between mechanical work done (W) and heat produced (H) is

$$W \propto H \text{ or } W = JH$$

where J is called mechanical equivalent of heat. Its value is $J = 4.184 \times 10^7 \text{ ergs} = 4.184 \text{ J}$.

Thus work done when 1 calorie of heat is produced = 4.184 J.

2. Work done by a gas for isothermal irreversible expansion from volume V_1 to volume V_2 against a constant external pressure P is;

$$W_{\text{irr}} = -P(V_2 - V_1) = -P\Delta V \quad (1 \text{ L atm} = 101.3 \text{ J})$$

3. According to first law of thermodynamics, $\Delta U = q + w$ where q is the heat absorbed by the system and w is the work done on the system.

4. Sign conventions for ΔU , q and w

If energy is absorbed by the system, i.e., internal energy increases, ΔU is positive.

If energy is released, i.e., internal energy of the system decreases, ΔU is negative.

If work is done on the system, w is positive.

If work is done by the system, w is negative.

If heat is absorbed by the system, q is positive.

If heat is given out by the system, q is negative.

5. $\Delta H_{\text{Reaction}}^\ominus = \sum \Delta H_f^\ominus(\text{Products}) - \sum \Delta H_f^\ominus(\text{Reactants})$.

6. $\Delta H_{\text{Reaction}}^\ominus = \sum \text{B.E. of Reactants} - \sum \text{B.E. of Products}$.

7. Enthalpy, $H = U + PV$

Enthalpy change, $\Delta H = \Delta U + P\Delta V$

8. Heat capacity, $C = \frac{q}{T_2 - T_1}$

where q is the heat absorbed to raise the temperature from T_1 and T_2 .

9. $C_V = (\partial U / \partial T)_V$ and $C_P = (\partial H / \partial T)_P$.

10. $C_P - C_V = R$.

11. Work done in isothermal reversible expansion,

$$w_{\text{max}} = -2.303 nRT \log(V_2/V_1) = -2.303 nRT \log(P_1/P_2)$$

(This is the maximum work obtained in an isothermal reversible expansion.)

12. For reversible adiabatic expansion, $PV^\gamma = \text{constant}$.

$$TV^{\gamma-1} = \text{constant}$$

and $TP^{(1-\gamma)/\gamma} = \text{constant}$, where $\gamma = C_P/C_V$.

13. Work done during adiabatic expansion of n moles of an ideal gas = $n C_V(T_2 - T_1)$.

14. $q_V = \Delta U$ and $q_P = \Delta H$

15. $q_P = q_V + \Delta n_g RT$ or $\Delta H = \Delta U + \Delta n_g RT$ where $\Delta n_g = n_P - n_R$.

16. Kirchoff's equation is $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$ and $\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V$.

17. Change in internal energy (for combustion) is determined by Bomb calorimeter.

$$\Delta U = C \times \Delta t \times \frac{Mw}{m}$$

where C = heat capacity of the calorimeter, $\Delta t = (t_2 - t_1)$ = rise in temperature, m = mass of the substance taken, and Mw = molecular mass of the substance.

18. Efficiency of heat engine, $\eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$

where q_2 = heat absorbed by the system at temperature T_2 of the source, q_1 = heat rejected by the system at temperature T_1 of the sink and W = net work done.

19. Entropy change, $\Delta S = q_{\text{rev}}/T$.

20. $\Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq 0$, where sign '=' refers to a reversible process (equilibrium) and sign '>' to an irreversible process (spontaneous process).

21. $\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_f$ and $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T_b$.

22. Entropy change of an ideal gas (for 1 mole)

$$\begin{aligned}\Delta S &= 2.303 \left(C_V \log \frac{T_2}{T_1} + R \log \frac{V_2}{V_1} \right) \\ &= 2.303 \left(C_P \log \frac{T_2}{T_1} + R \log \frac{P_1}{P_2} \right)\end{aligned}$$

At constant temperature (*isothermal process*)

$$\Delta S = 2.303 R \log \frac{V_2}{V_1} = 2.303 R \log \frac{P_1}{P_2}$$

At constant volume (*isochoric process*)

$$\Delta S = 2.303 C_V \log \frac{T_2}{T_1}$$

At constant pressure (*isobaric process*)

$$\Delta S = 2.303 C_P \log \frac{T_2}{T_1}$$

23. Gibb's energy, $G = H - TS$

Gibb's energy change, $\Delta G = \Delta H - T\Delta S$.

24. $\Delta G^\ominus = \Sigma G^\ominus(\text{Products}) - \Sigma G^\ominus(\text{Reactants})$.

25. $\Delta S^\ominus = \Sigma S^\ominus(\text{Products}) - \Sigma S^\ominus(\text{Reactants})$.

26. If ΔG is negative, process is spontaneous.

If ΔG is positive, process is non-spontaneous.

If ΔG is zero, process is in equilibrium.

27. $\Delta G = W_{\text{useful}}$

28. **Clausius-Clapeyron equation:** For Liquid \rightleftharpoons Vapour equilibrium,

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where P_1 and P_2 are vapour pressures at temperatures T_1 and T_2 respectively or P_1 and P_2 are the pressures at which the boiling points are T_1 and T_2 respectively and ΔH_v is latent heat of vapourisation.

29. The criterion for equilibrium is

$$\Delta_r G = 0$$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^\ominus$ is related to equilibrium constant of the reaction as follows:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln k$$

$$0 = \Delta_r G^\ominus + RT \ln k$$

or $\Delta_r G^\ominus = -2.303 RT \log k$

Note: At equilibrium, $\Delta_r G = 0$, but $\Delta_r G^\ominus \neq 0$.

30. $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$

31. **Total differential equation:** $dG = VdP - SdT$

32. At constant temperature, T

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

At constant pressure, P

$$\left(\frac{\partial G}{\partial P} \right)_P = -S$$

Chemical processes are accompanied either by absorption or by evolution of energy. For example, removing an electron from hydrogen atom, breaking a carbon hydrogen bond, forming calcium oxide and CO_2 from calcium carbonate etc., all proceed with absorption of energy. On the other hand, burning of carbon and reaction of hydrogen and oxygen proceed with the evolution of energy. The chemical energy may also be used to do mechanical work or to provide electrical energy through a galvanic cell such as dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics.

Thermodynamics is derived from Greek words 'therme' and 'dynamis'. Its literal meaning is motion or flow (dynamics) of heat (thermos). However, the term is used in a more general way. Thermodynamics is a branch of science that deals with the quantitative relationship between heat and other forms of energies. When we confine our study to thermodynamics of chemical processes, it is referred to as chemical thermodynamics.

Thermodynamics is not concerned with the total energy of the body but only with energy changes taking place during the transformation. The study of thermodynamics is based on three generalisations derived from experimental results. These generalisations are known as first, second, and third law of thermodynamics based on human experience and there is no formal proof for them. Scientists are of the view that nothing contrary to these laws will ever occur.

Scope and limitations of thermodynamics

The importance of thermodynamics is:

- Predicts the feasibility of the chemical reaction under the given set of conditions.
- Predicts the extent to which the chemical reaction can occur before the equilibrium is attained.
- Provides the explanation of the macroscopic (i.e., bulk) properties of matter in terms of the concepts that are supported by the microscopic views of our material world.

Most important laws of physical chemistry such as Raoult's law, van't Hoff law, distribution law, phase rule, law of equilibrium, laws of thermochemistry and expression for elevation in boiling point and depression in freezing point are in accordance with laws of thermodynamics.

Limitations of thermodynamics: (a) The laws of thermodynamics apply only to the matter in bulk, i.e., macroscopic system and not to individual atoms or molecules of the macroscopic system. Thermodynamics does not deal with internal structure of atoms and molecules. (b) Thermodynamics can only predict the feasibility or spontaneity of a process under a given set of conditions but does not tell anything about the rate at which the given process may proceed. It is only concerned with initial and final states of the system. For example, thermodynamics predicts that the reaction between oxygen and hydrogen is possible under ordinary conditions but does not tell whether the reaction is fast or slow.

In this unit, we would like to answer some of the important questions through thermodynamics such as:

- How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?
- What drives a chemical reaction/process?
- To what extent do the chemical reactions proceed?

6.2 THERMODYNAMIC TERMS

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

6.2.1 THE SYSTEM AND THE SURROUNDINGS

- System:** A system may be defined as any specified portion of matter under study which is separated from the rest of the universe with a bounding surface. A system may consist of one or more substances.
- Surroundings:** The rest of the universe that might be in a position to exchange energy and matter with the system is called the surroundings. In simple cases, surroundings generally imply air, or water-bath in which a system under examination is immersed.

The surroundings include everything other than the system. The system and the surroundings together constitute the universe.

Thus,

$$\text{Universe} = \text{System} + \text{Surroundings}$$

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances *A* and *B* kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 6.1).

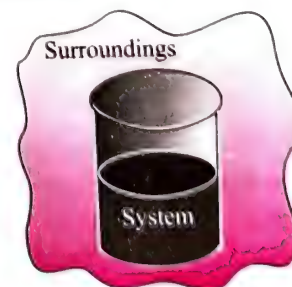


Fig. 6.1 System and the surroundings

Note that the system may be defined by physical boundaries, such as beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of

wall which may be real or imaginary. The wall that separates the system from the surroundings is called *boundary*. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

Types of the System

We further classify the systems according to the movements of matter and energy in or out of the system.

- a. Open system:** In an open system, there is exchange of energy and matter between the system and the surroundings [Fig. 6.2(a)]. The presence of reactants in an open beaker is an example of an open system. Here the boundary is an imaginary surface enclosing the beaker and the reactants.
- b. Closed system:** In a closed system, there is no exchange of matter, but exchange of energy is possible between the system and the surroundings [Fig. 6.2(b)]. The presence of reactants in a closed vessel made of conducting material, e.g., copper or steel, is an example of a closed system.

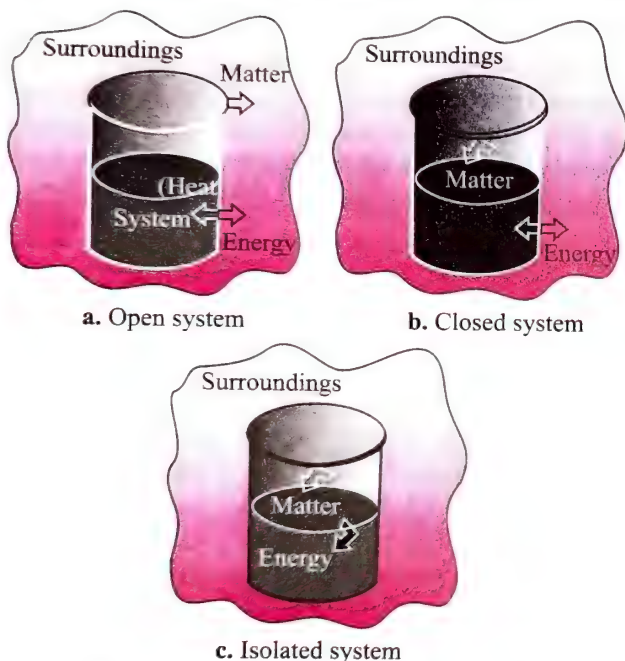


Fig. 6.2 Open, closed, and isolated systems

- c. Isolated system:** In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 6.2(c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

On the basis of composition, there are two types of systems:

- a. Homogeneous system:** A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one phase only. Examples are: a pure single solid, liquid or gas, mixture of gases and a true solution.
- b. Heterogeneous system:** A system is said to be heterogeneous when it is not uniform throughout, i.e., it consists two or more phases. Examples are ice in contact with water, two or more immiscible liquids, insoluble solids in contact with a liquid, a liquid in contact with vapour, etc.

Macroscopic Properties of the System

Thermodynamics deals with matter in terms of bulk (large number of chemical species) behaviour. *The properties of the system which arise from the bulk behaviour of matter are called macroscopic properties.* The common examples of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index, etc.

The macroscopic properties can be subdivided into two types:

- a. Intensive properties**
- b. Extensive properties**
 - a. Intensive properties:** The properties that do not depend upon the quantity of matter present in the system or size of the system are called intensive properties. For example temperature (T), pressure (P), concentration, density, dipole moment, refractive index, surface tension, molar volume, gas constant (R) specific heat capacity, vapour pressure, specific gravity, dielectric constant, and emf of a dry cell.
 - b. Extensive properties:** The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties. For example, volume, energy, heat capacity, enthalpy, entropy, free energy, length, and mass.

It may be noted that *the ratio of the two extensive properties becomes intensive in nature.* For example, mass and volume are extensive properties, but the ratio of mass/volume, i.e., density, is intensive; it is independent of quantity of matter. Similarly, heat capacity is extensive, but molar heat capacity is intensive. In general, if x is any extensive property of n mol of system, the molar property of the system x_m is intensive because it refers to the property of 1 mol of the system and is independent of the quantity of matter: $x_m = x/n$.

6.2.2 STATE OF SYSTEM AND STATE VARIABLES

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (P), volume (V), and the temperature (T) as well as the composition of the system.

The condition of a system is referred as its *state* and the measurable properties required to describe the state of the system are called *state variables* or *state functions*. These variables are inter-related with each other and by assigning two or three of these variables, others are automatically fixed.

6.2.3 STATE FUNCTION AND PATH FUNCTION

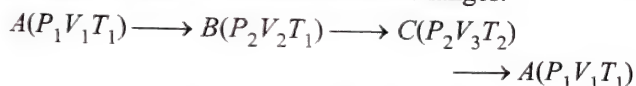
A physical quantity is said to be a *state function* if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained. For example, a person standing on the roof of a five-storeyed building has a fixed potential energy, irrespective of the fact whether he reached there by stairs or by lift. Thus, the potential energy of the person is a state function. On the other hand, the work done by the legs of the person to reach the same height is not same in the two cases, i.e., whether he went by lift or by stairs. Hence, work is a *path function*.

6.2.4 THERMODYNAMIC PROCESS

A process is the path along which a change of state takes place. The process can occur under a variety of conditions which must be defined because many things may depend on the nature of the process.

The various types of the process are:

- Isothermal process:** The process is termed *isothermal* if temperature remains fixed, i.e., operation is done at constant temperature. This can be achieved by placing the system in a constant temperature bath, i.e., thermostat. For an isothermal process, $dT = 0$, i.e., heat is exchanged with the surroundings and the system is not thermally isolated.
- Adiabatic process:** If a process is carried out under such condition that no exchange of heat takes place between the system and the surroundings, the process is termed *adiabatic*. The system is thermally isolated, i.e., $dQ = 0$. This can be done by keeping the system in an insulated container, i.e., thermos flask. In adiabatic process, the temperature of the system varies.
- Isobaric process:** The process is known as *isobaric* in which the pressure remains constant throughout the change, i.e., $dP = 0$.
- Isochoric process:** The process is termed as *isochoric* in which volume remains constant throughout the change, i.e., $dV = 0$.
- Cyclic process:** When a system undergoes a number of different processes and finally returns to its initial state, it is termed *cyclic process*. For a cyclic process $dE = 0$, $dH = 0$. For example, in a process shown below, the system returns to the original state A after successive changes.



The graphical representation of various chemical processes w.r.t. pressure volume behaviour of given amount of ideal gas has been shown in Fig. 6.3.

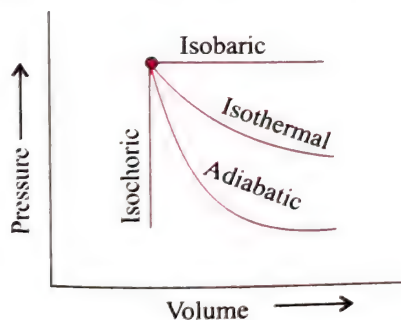


Fig. 6.3 Graphic representation of various thermodynamic process.

REVERSIBLE AND IRREVERSIBLE PROCESS

The terms reversible and irreversible refer to the path or manner in which the process is carried out.

- Reversible process:** A process which occurs infinitesimally slowly, i.e., opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be a *reversible process*. In fact, a reversible process is considered to proceed from initial state to final state through an infinite series of

infinitesimally small stages and at every stage it is virtually in state of equilibrium. A reversible process is an ideal process and cannot be realised in practice.

- Irreversible process:** When the process goes from initial to final state in a single step in finite time and cannot be reversed, it is termed as *irreversible process*. In such a case, equilibrium state exists only at the initial and final stages of the process. An irreversible process is spontaneous in nature. It is real and can be performed in practice. All natural processes are irreversible in nature.

Table 6.1 Difference between reversible and irreversible processes

Reversible process	Irreversible process
a. It is an ideal process and takes infinite time.	a. It is a spontaneous process and takes finite time.
b. The driving force is infinitesimally greater than the opposing force.	b. The driving force is much greater than the opposing force.
c. It is at equilibrium at all stages.	c. Equilibrium exists in the initial and final stages only.
d. Work obtained is maximum	d. Work obtained is not maximum.
e. It is difficult to realise in practice.	e. It can be performed in practice.

6.2.5 INTERNAL ENERGY AS A STATE FUNCTION

As pointed out earlier the chemical reactions are accompanied by the energy changes, we need to introduce a quantity which represents the total energy of the system. It may be chemical electrical, mechanical, or any other type of energy, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, (U) of the system, which may change when

- heat passes into or out of the system.
- work is done on or by the system.
- matter enters or leave the system.

Internal Energy (U) and Change in Internal Energy (ΔU)

Every substance possesses a fixed quantity of energy which depends upon its chemical nature and its state of existence. This is known as *intrinsic energy* or *internal energy* and is denoted by the symbol U . Every substance has a definite value of internal energy and is made up of kinetic energy and potential energy of the constituent particles namely atoms, ions, or molecules. The kinetic energy is due to the motion of all particles and the potential energy arises due to different types of interactions between the particles and is equal to the energies possessed by all its constituents namely atoms, ions, or molecules. The various forms of energies which contribute towards the internal energy are *translational energy, rotational energy, vibrational energy, electronic energy, nuclear energy of constituent atoms, potential energy of the molecules due to molecular interactions, chemical bond energy due to existence of bonds between atoms within the molecules*, etc. The sum of these different forms of energies associated with the molecules is called its internal energy.

$$U_{\text{Total}} = U_{\text{Translational}} + U_{\text{Rotational}} + U_{\text{Vibrational}} + U_{\text{Bonding}} + U_{\text{Electronic}} + \dots$$

Different substances have different values of internal energy. For example, the internal energy of 1 mole of CO_2 at NTP is different from the internal energy of 1 mole of SO_2 under similar conditions of temperature and pressure. It may be noted that the absolute value of internal energy of a substance cannot be calculated because it is not possible to determine the exact value for the constituent energies such as translational, vibrational, rotational energy, etc. However, we are interested mostly in change in internal energy which occurs during chemical reactions. The change in internal energy of a reaction may be considered as the difference between the internal energies of the two states.

Let U_A and U_B are the internal energies in states A and B , respectively. Then the difference between the internal energies in the two states will be

$$\Delta U = U_B - U_A$$

The difference in internal energies (ΔU) has a fixed value and will be independent of the path taken between two states A and B . For the chemical reactions, the change in internal energy may be considered as the difference between the internal energies of the products and that of the reactants, i.e.,

$$\Delta U = U_{\text{Products}} - U_{\text{Reactants}}$$

Thus, the internal energy, U is a *state function*. This means that ΔU depends only on the initial and final states and is independent of the path. In other words, ΔU will be same even if the change is brought about differently.

ΔU is positive if $U_P > U_R$, thus $\Delta U > 0$. If $U_P < U_R$, $\Delta U < 0$ or sign of ΔU is negative.

Characteristics of internal energy

- Internal energy of a system is an extensive property
- Internal energy is a state function.
- The change in the internal energy does not depend on the path by which the final state is reached.
- There is no change in internal energy in a cyclic process.
i.e., $\Delta U_{\text{cyclic}} = 0$
- Internal energy depends on temperature, pressure, volume and quantity of matter.
- The internal energy (or intrinsic energy) cannot be calculated. By convention, the internal energy of an element in most stable form, is zero.
- Internal energy change (ΔU) per mole is calculated by using the formula (from Bomb calorimeter)

$$\Delta U = \frac{C \times \Delta T \times Mw}{m}$$

where C = heat capacity of the calorimeter system (including water)
 ΔT = rise in temperature
 Mw = molar mass of the substance and
 m = amount of the substance taken.

6.2.6 HEAT (q)

Heat is a form of energy. It flows from one system to another because of the difference in temperature. Heat flows from higher

temperature to lower temperature. Energy is also exchanged between a system and its surroundings by heat transfer. The exchange of heat occurs through the thermally conducting walls which constitute boundary between system and surrounding. The energy transfer continues till the system and the surrounding attain the same temperature. If the system is at lower temperature than the surroundings, the energy is gained by the system from the surroundings causing a rise in the temperature of the system. The amount of heat gained or lost by the system is represented by q . According to the international conventions,

Heat absorbed by the system is positive, i.e., $q > 0$.

Heat given out by the system is negative, i.e., $q < 0$.

6.2.7 WORK (w)

Work is a mode of energy transfer to or from a system with reference to the surroundings. If an object is displaced through a distance dx against a force of F , then the amount of work done is defined as

$$w = F \times dx$$

There are many types of work and all of them could be expressed as the product of two factors:

- An intensity factor
- A capacity factor

Some of them are:

- Gravitational work = $(mg) \times h$
where m = mass of body, g = acceleration due to gravity, h = height moved.
- Electrical work = $Q \times V$
where Q = charge, V = potential gradient.
- Mechanical work = $P_{\text{ex}}(V_2 - V_1) = P_{\text{ex}} \Delta V$
where P_{ex} = external pressure, ΔV = increase or decrease in volume.

Work associated with change in volume of a system against external pressure is called mechanical work.

P_{ex} = intensity factor

ΔV = capacity factor

Work (w) is a path-dependent function, it is manifestation of energy. Work done on a system increase the energy of the system and work done by the system decreases the energy of the system.

Work done on the system, $w = +ve$

Work done by the system, $w = -ve$

Units of work. In CGS unit, the work is expressed in ergs but in SI unit, work is expressed in Joules. The equivalence between joules and other units of work is

$$1 \text{ J} = 10^7 \text{ ergs} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

The common forms of work that we come across in the study of the thermodynamics are:

- Pressure-volume work
- Electrical work

a. Pressure-volume (P - V) work: This type of work is also called expansion work and it is significant in systems which

consist of gases and involve changes in volume against the external pressure.

Expression for P-V work

It is the work done when the gas expands or contracts against the external pressure (usually atmospheric pressure). To understand this, consider a cylinder fitted with a frictionless and weightless piston having area of cross-section equal to A . Let it contains gas of volume V and let the pressure of gas inside in the cylinder is P .

When the internal pressure of the gas is slightly more than the external pressure, P_{ex} , the gas expands and the piston moves a very small distance dl . Then, change in volume is given by

$$\Delta V = A \cdot dl$$

$$\text{We know that Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$\text{or Force} = \text{Pressure} \times \text{Area}$$

Therefore, force on the piston

$$F = P_{\text{ex}} \times A.$$

$$\text{Force} = \text{Pressure} \times \text{Position Area} = P \cdot A$$

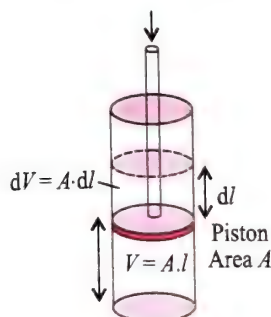


Fig. 6.4 Pressure-volume work

If the small work done by the movement of the piston is dw ,

$$\text{Work} = \text{Force} \times \text{Distance}$$

$$dw = -P_{\text{ex}} \times A \, dl$$

Negative sign is used for work done by system as convention; (discussed later).

But $A \times dl = dV$ is a small change in volume of the gas so that

$$dw = -P_{\text{ex}} \cdot dV$$

Work done in irreversible process

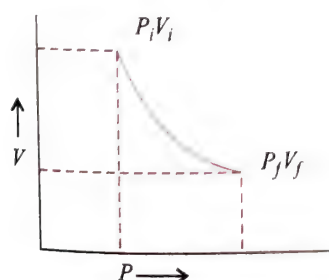


Fig. 6.5 Irreversible work done

If the volume of the system changes by a finite quantity from volume V_i to V_f , then total work done w can be obtained by

integrating $-P \cdot dV$ (when P is constant) over the volume change from V_i to V_f . Thus

$$\begin{aligned} w &= - \int_{V_i}^{V_f} P_{\text{ex}} \, dV \\ &= -P_{\text{ex}} (V_f - V_i) \\ &= -P_{\text{ex}} \Delta V \quad (\because \Delta V = V_f - V_i) \end{aligned}$$

If the external pressure (P_{ex}) is slightly more than the pressure of the gas, the gas will contract, i.e., the work will be done by the surroundings on the system. In that case, V_f will be less than V_i and ΔV is negative.

$$\therefore w = p \Delta V$$

Thus,

- If the gas expands, $V_f > V_i$ and work is done by the system and w is negative.
- If the gas contracts, $V_f < V_i$ and work is done on the system and w is positive.

Work done in isothermal reversible expansion or compression of an ideal gas

In reference to the above example, we know that $w = -P \cdot \Delta V$. Let us now assume that the external pressure is not constant and changes in finite number of steps is going from volume V_i to V_f , then the net work done is given by summation of $-P \cdot \Delta V$ terms over all the steps as shown in Fig. 6.6(a) and is represented as

$$w = -\Sigma P \cdot \Delta V$$

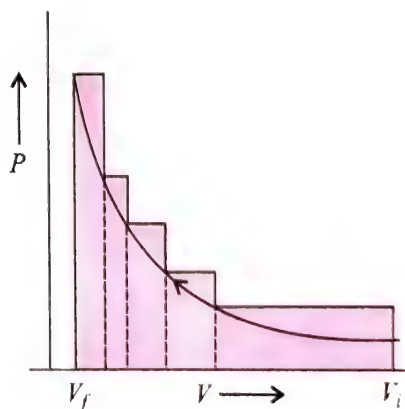


Fig. 6.6(a) PV plot when pressure is not constant and changes in finite steps during compression from initial volume V_i to final volume V_f . Work done on the gas is represented by the shaded area

Let us now assume further that the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV . In such a case, we can calculate the work done on the gas by the relation

$$w = - \int_{V_i}^{V_f} P_{\text{ex}} \, dV$$

Here, P_{ex} at each state is equal to $(P_{\text{in}} + dP)$ in case of compression [Fig. 6.6(b)]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $P_{\text{ex}} = (P_{\text{in}} \pm dP)$. Such processes are called reversible processes.

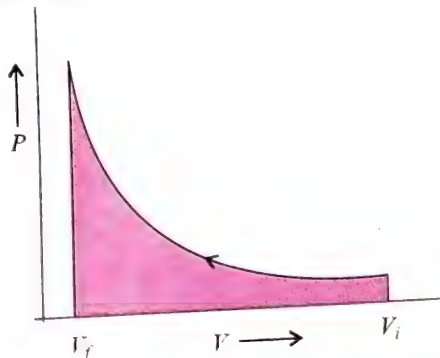


Fig. 6.6(b) pV plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume V_i to final volume V_f . Work done on the gas is represented by the shaded area

We can relate work to internal pressure of the system under reversible conditions by writing above equation as follows:

$$w_{\text{rev}} = - \int_{V_i}^{V_f} P_{\text{ex}} dV = - \int_{V_i}^{V_f} (P_{\text{in}} \pm dP) dV$$

Since $dP \times dV$ is very small we can write

$$w_{\text{rev}} = - \int_{V_i}^{V_f} P_{\text{in}} dV$$

Now, the pressure of the gas (P_{in} which we can write as P now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas, i.e., $PV = nRT$

$$\Rightarrow P = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{\text{rev}} = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -2.303nRT \log \frac{V_f}{V_i} \text{ or } -2.303RT \log \frac{P_i}{P_f}$$

Free expansion: Expansion of a gas in vacuum ($p_{\text{ex}} = 0$) is called free expansion. No work is done during free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

w_{rev} is maximum work: Work done during isothermal expansion of ideal gas is given by the equation as:

$$w = -P_{\text{ex}} \Delta V$$

Now, for a given change of volume (ΔV), w can be maximum if P_{ex} is maximum. But for expansion P_{ex} has to be smaller than P_{in} . This means that for getting maximum work, the external pressure has to be infinitesimally smaller than the internal pressure of the gas. These conditions are nearly close to reversibility. Thus, we can write that for a given change of volume,

$$w_{\text{rev}} = w_{\text{max}}$$

Isothermal expansion and compression of an ideal gas and relationship between different thermodynamic quantities

Process	Expansion	Compression	Cyclic
Reversible $q, (-w)$ $\Delta U, \Delta H$	$w = -2.303 nRT \log \frac{V_2}{V_1}$ 0	$w = 2.303 nRT \log \frac{V_2}{V_1}$ 0	0 0
Free $q, (-w)$ $\Delta U, \Delta H$	0 0	$P_{\text{ex}}(V_1 - V_2) < 2.303nRT \log \frac{V_1}{V_2}$ 0	$P_{\text{ex}}(V_1 - V_2) < 0$ 0
Intermediate $q, (-w)$ $\Delta U, \Delta H$	$0 < P_{\text{ex}}(V_2 - V_1) < 2.303nRT \log \frac{V_2}{V_1}$ 0	$P_{\text{ex}}(V_1 - V_2) < 2.303nRT \log \frac{V_1}{V_2}$ 0	$P_{\text{ex}}(V_2 - V_1) < 0$ 0

Maximum work is done in reversible isothermal expansion process.

Note:

1. Sign conventions

If work is done on the system, W is positive.

If work is done by the system, W is negative.

If heat is absorbed by the system, q or ΔH is positive.

If heat is given out by the system, q or ΔH is negative.

If energy is absorbed by the system i.e., internal energy increases, ΔU is positive.

If energy is released i.e., internal energy of the system decreases, ΔU is negative.

2. Pressure-volume work done in an isothermal irreversible expansion.

$$W_{\text{irr}} = -P_{\text{ext}} \Delta V$$

3. Pressure-volume work done in an isothermal reversible expansion,

$$W_{\text{rev}} = -2.303 nRT \log \frac{V_2}{V_1} = -2.303 nRT \log \frac{P_1}{P_2}$$

4. For an isothermal reversible process

$\Delta U = 0$, (it is because internal energy is function of temperature)

$$q = -W \quad \left[\text{Since } W = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} \right]$$

$$\text{or } q = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta PV$$

$$\Delta H = \Delta U + \Delta nRT$$

For an isothermal expansion, $\Delta T = 0$ (R and n are constants)

$$\Delta H = \Delta U = 0$$

5. For an isothermal isobaric expansion. At constant T and P

$$q = -W$$

$$\Delta U = 0, \Delta H = 0$$

6. For an isochoric process

$$\Delta V = 0 \quad \therefore \quad q = \Delta U$$

7. For an adiabatic process

$$q = 0 \quad \therefore \quad \Delta U = W$$

8. For a cyclic process

$$\Delta U = 0 \quad \therefore \quad q = -W$$

9. For an adiabatic reversible expansion of gas

$$\text{a. } TV^{\gamma-1} = \text{constant}$$

$$\text{b. } TP^{(1-\gamma)/\gamma} = \text{constant}$$

$$\text{c. } PV^{\gamma} = \text{constant}$$

10. Both q and W are not state functions since their values depend upon the path by which the change is carried, but, the quantity q + W is a state function. This is because q + W = ΔV and ΔU is a state function.

QUESTIONS BASED ON WORK (W) HEAT (q) AND INTERNAL ENERGY (U)

ILLUSTRATION 6.1

- I. A process in which pressure remains constant is called
 - a. Isochoric process
 - b. Isothermal process
 - c. Adiabatic process
 - d. Isobaric process
- II. Which one of the following is a state property/function?
 - a. Heat
 - b. Work
 - c. Internal energy
 - d. Potential energy
- III. Which of the following is an extensive property?
 - a. Enthalpy
 - b. Concentration
 - c. Density
 - d. Viscosity
- IV. If temperature of the system remains constant during the course of change, the change is
 - a. Isothermal
 - b. Adiabatic
 - c. Isobaric
 - d. Isochoric

Sol.

- I. d. Isobaric process ($\Delta P = 0$).
- II. c. Internal energy is state function.

III. a. Enthalpy depends upon the quantity of substance.

IV. a. In isothermal process, temperature remains constant ($\Delta T = 0$).

ILLUSTRATION 6.2

- I. A process in which volume remains constant is called
 - a. Isochoric process
 - b. Isothermal process
 - c. Adiabatic process
 - d. Isobaric process
- II. Identify intensive property from the following
 - a. Volume
 - b. Mass
 - c. Enthalpy
 - d. Temperature
- III. Which of the following is an extensive property of the system?
 - a. Refractive index
 - b. Viscosity
 - c. Temperature
 - d. Volume
- IV. An isolated system is that system in which
 - a. There is not exchange of energy with the surroundings.
 - b. There is exchange of mass and energy with the surroundings.
 - c. There is no exchange of energy and mass with the surroundings.
 - d. There is exchange of mass with the surroundings.

Sol.

- I. a. Isochoric process ($\Delta V = 0$).
- II. d. Temperature is independent of the mass of substance.
- III. d. Volume depends upon mass of substance.
- IV. c. In isolated systems neither heat nor matter can be exchanged.

ILLUSTRATION 6.3

- I. Thermodynamics is concerned with
 - a. Total energy of a system
 - b. Energy changes in a system
 - c. Rate of a chemical change
 - d. Mass changes in nuclear reactions
- II. Internal energy of a system of molecules is determined by taking into consideration its
 - a. Kinetic energy
 - b. Vibrational energy
 - c. Rotational energy
 - d. All kinds of energies present in the molecules
- III. A thermodynamic quantity is that
 - a. Which is used in thermochemistry.
 - b. Which obeys all laws of thermodynamics.
 - c. Quantity whose value depends only upon the state of the system.
 - d. Quantity which is used in measuring thermal change.
- IV. Thermodynamic equilibrium involves
 - a. Chemical equilibrium
 - b. Thermal equilibrium
 - c. Mechanical equilibrium
 - d. All the three

V. For an adiabatic process, which of the following relations is correct?

- a. $\Delta U = 0$ b. $P \Delta V = 0$ c. $q = 0$ d. $q = +w$

Sol.

- I. b. Energy changes in a system.
 II. d. All kinds of energies present in the molecules.
 III. c.
 IV. d.
 V. c. $q = 0$ (Adiabatic process)

ILLUSTRATION 6.4

Express the change in internal energy of a system when

- No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?
- No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?
- w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Sol.

- $\Delta U = W_{ad}$, wall is adiabatic
- $\Delta U = -q$, thermally conducting walls
- $\Delta U = q - w$, closed system.

ILLUSTRATION 6.5

Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion?

Sol. We have $q = -w = p_{ex}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

ILLUSTRATION 6.6

Consider the same expansion but this time against a constant external pressure of 1 atm.

Sol. We have $q = -w = p_{ex}(8) = 8 \text{ litre-atm}$

ILLUSTRATION 6.7

Consider the same expansion, to a final volume of 10 litres conducted reversibly.

Sol. ($PV = nRT = 1 \text{ atm} \times 10 \text{ L} = 10 \text{ atm L}$)

$$\begin{aligned} q = -w &= 2.303 nRT \log \frac{V_2}{V_1} \\ &= 2.303 \times 10 \text{ atm L} \log \frac{10}{2} \\ &= 16.1 \text{ atm L} \end{aligned}$$

ILLUSTRATION 6.8

Two litres of N_2 at 0°C and 5 atm pressure is expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 L.

Assuming gas to be ideal, calculate the work of expansion.

Sol.

Since, the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$$\therefore W = -P_{ex}(V_2 - V_1)$$

$$W = -1 \times (V_2 - V_1)$$

$$\text{Given, } V_1 = 2 \text{ L } V_2 = ? \quad T = 273 \text{ K}$$

$$P_1 = 5 \text{ atm} \quad P_2 = 1 \text{ atm}$$

$$\therefore P_1 V_1 = P_2 V_2$$

$$\therefore V_2 = \frac{2 \times 5}{1} = 10 \text{ L}$$

$$\therefore W = -1 \times (10 - 2) = -8 \text{ L-atm}$$

$$\begin{aligned} &= -\frac{8 \times 1.987}{0.0821} \text{ cal} = -\frac{8 \times 1.987 \times 4.184}{0.0821} \text{ J} \\ &= 810.10 \text{ J} \end{aligned}$$

ILLUSTRATION 6.9

Calculate the work done when 1.0 mol of water at 373 K vaporises against an atmospheric pressure of 1.0 atm. Assume ideal gas behaviour.

Sol.

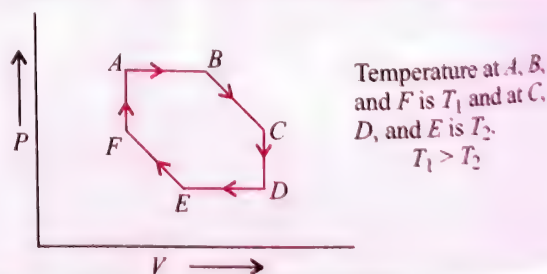
The volume occupied by water is very small and thus the volume change is equal to the volume occupied by 1 g mol of water vapour.

$$V = \frac{nRT}{P} = \frac{1.0 \times 0.0821 \times 373}{1.0} = 31.0 \text{ L}$$

$$\begin{aligned} W &= -P_{ext} \times \Delta V = -(1.0) \times (31.0) \text{ L-atm} \\ &= -(31.0) \times 101.3 \text{ J} = -3140.3 \text{ J} \end{aligned}$$

ILLUSTRATION 6.10

Identify different steps in the following cyclic process:



Sol.

- $A \rightarrow B$: Temperature and pressure are constant. Therefore, it is an isothermal and isobaric process.
- $B \rightarrow C$: It is adiabatic expansion in which temperature falls from T_1 to T_2 .
- $C \rightarrow D$: Temperature and volume are constant. Therefore, this process is isothermal and isochoric.
- $D \rightarrow E$: Temperature and pressure are constant. Therefore, it is an isothermal and isobaric contraction.

- e. $E \rightarrow F$: It is adiabatic compression in which temperature increases from T_2 to T_1 .
- f. $F \rightarrow A$: Temperature and volume are constant. Therefore, it is an isothermal and isochoric process.

ILLUSTRATION 6.11

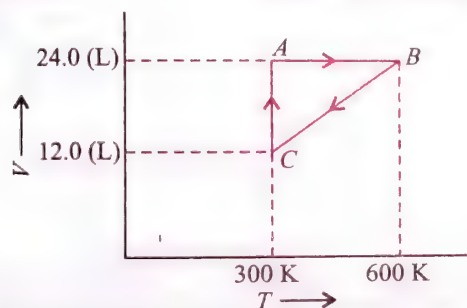
A gas expands by 0.5 L against a constant pressure of 1 atm. Calculate the work done in joule and calorie.

Sol. $\text{Work} = -P_{\text{ex}} \times \text{Volume change}$
 $= -1 \times 0.5 = -0.5 \text{ L atm}$
 $= -0.5 \times 101.328 \text{ J} = -50.664 \text{ J}$
 $0.5 \text{ L atm} = -0.5 \times 24.20 \text{ cal} = -12.10 \text{ cal}$

ILLUSTRATION 6.12

One mole of an ideal gas is put through a series of changes as shown in the graph in which A, B, and C mark the three stages of the system. At each stage the variables are shown in the graph.

- Calculate the pressure at three stages of system.
- Name the processes during the following changes:
 - A to B
 - B to C
 - C to A
 - Overall change

**a. At stage A:**

$$V = 24.0 \text{ L}; T = 300 \text{ K}; n = 1;$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

Substituting these values in the ideal gas equation,

$$PV = nRT$$

$$P = \frac{1 \times 0.0821 \times 300}{24.0} = 1.026 \text{ atm}$$

At stage B: Volume remains the same but temperature changes from 300 K to 600 K. Thus, according to gaseous law, the pressure will be doubled at B with respect to A.

$$\text{Pressure at B} = 2 \times 1.026 = 2.052 \text{ atm}$$

At stage C: Temperature is 300 K and volume is half that of stage A. Thus, according to Boyle's law, the pressure at C will be doubled with respect to A.

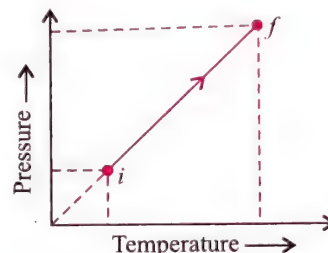
$$\text{Pressure at C} = 2 \times 1.026 = 2.052 \text{ atm}$$

- During the change from A to B, volume remains constant, the process is *isochoric*.
 - During the change from B to C, pressure remains constant, the process is *isobaric*.

- During the change from C to A, temperature remains constant, the process is *isothermal*.
- Overall, the process is *cyclic* as it returns to initial state.

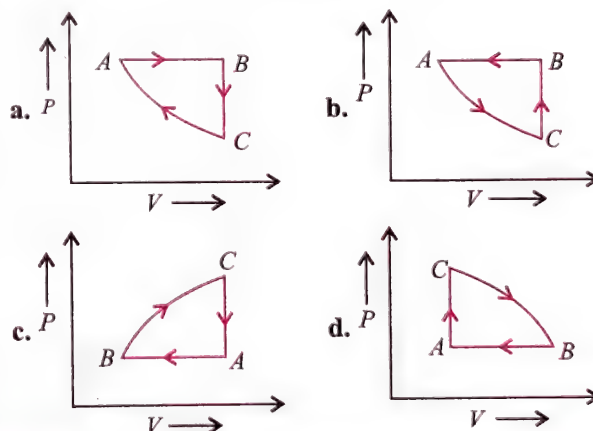
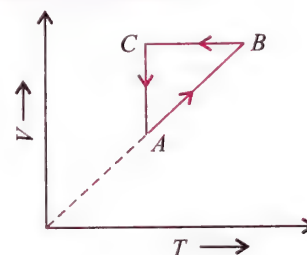
ILLUSTRATION 6.13

- A thermodynamic system consists of a cylinder-piston arrangement with ideal gas in it. It goes from the state *i* to the state *f* as shown in the figure. The work done by the gas during the process is



- Zero
- Negative
- Positive
- Nothing can be predicted

- A cyclic process ABCA is shown in a V-T diagram. The corresponding P-V diagram is



- Which one of the following statements about state functions is correct?

- Internal energy, enthalpy, heat, and work are all thermodynamic state functions.
- A state function depends both on the past history of a system and on its present condition.
- The state function describing a system of equilibrium change with time.
- The difference in a state function for any process depends only on the initial and final states.

Sol.

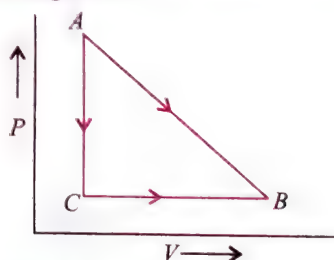
- $P \propto T$, so volume is constant. So this is isochoric process in which work is always zero.

II. a. As $P \propto \frac{1}{V}$ (Boyle's law)

III. d. State function does not depend upon the path of the process.

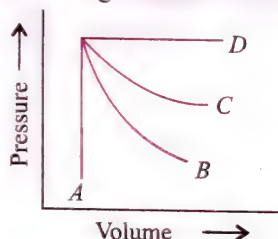
ILLUSTRATION 6.14

I. Consider the modes of transformations of a gas from state A to state B as shown in the given P-V diagram. Which one of the following is true?



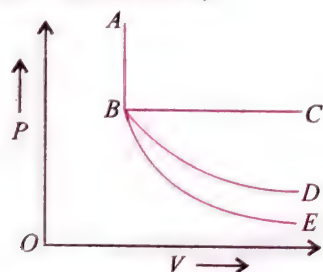
- a. $\Delta H = q$ along $A \rightarrow C$
 b. ΔS is same along both $A \rightarrow B$ and $A \rightarrow C \rightarrow B$
 c. w is same along both $A \rightarrow B$ and $A \rightarrow C \rightarrow B$
 d. $w > 0$ along both $A \rightarrow B$ and $A \rightarrow C \rightarrow B$

II. Which of the following statements is/are correct?

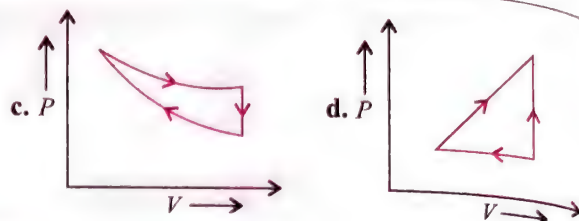
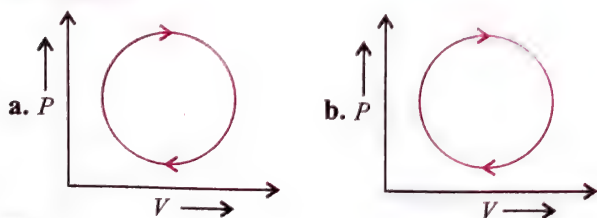


- a. A represents isochoric process
 b. B represents adiabatic process
 c. C represents isothermal process
 d. D represents isobaric process

III. In P-V diagram shown below,



- a. AB represents adiabatic process.
 b. AB represents isothermal process.
 c. AB represents isobaric process.
 d. AB represents isochoric process.
- IV. The following are the P-V diagrams for cyclic processes for a gas. In which of these processes, heat is not absorbed by the gas?



Sol.

I. c. Work (w) is a state function. It depends upon the initial and final state of system.

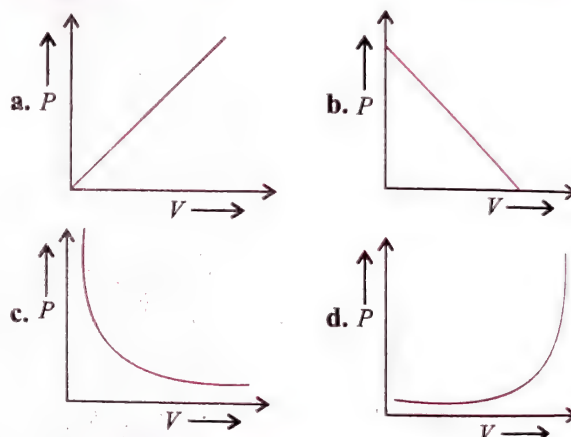
II. a, b, c, d

III. d. In AB process, volume does not change hence it is isochoric process.

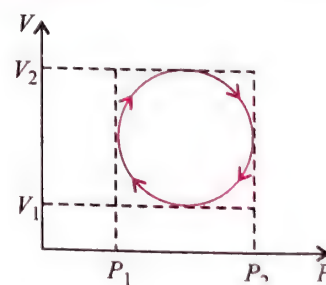
IV. d. In (d) process is not cyclic.

ILLUSTRATION 6.15

I. The graph between P and V at constant temperature should look like

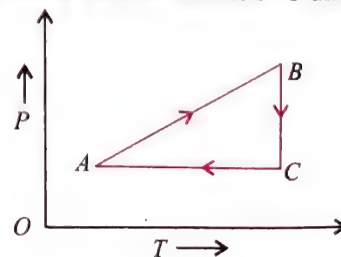


II. In the cyclic process shown on P-V diagram, the magnitude of the work done is

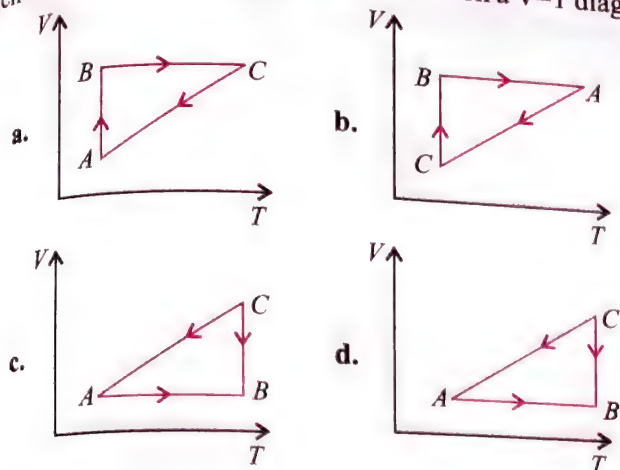


- a. $\pi \left(\frac{P_2 - P_1}{2} \right)^2$ b. $\pi \left(\frac{V_2 - V_1}{2} \right)^2$
 c. $\frac{\pi}{4} (P_2 - P_1) (V_2 - V_1)$ d. $\pi (P_2 V_2 - P_1 V_1)$

III. A cyclic process is shown in the P-T diagram.



Which of the curves shows the same process on a V-T diagram?



Sol.

I. c. $P \propto \frac{1}{V}$ (Boyle's law)

II. (a, b) Work done = Area under the curve

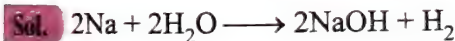
$$\begin{aligned} \text{Area of sphere} &= \pi r^2 = \pi \frac{(V_2 - V_1)^2}{2} \left(r = \frac{V_2 - V_1}{2} \right) \\ &= \frac{\pi(P_2^2 - P_1^2)}{2} \left(r = \frac{P_2 - P_1}{2} \right) \end{aligned}$$

\therefore (a) and (b)

III. c. as $P \propto \frac{1}{V}$ (Boyle's law).

ILLUSTRATION 6.16

Calculate the work done in open vessel at 300 K, when 92 g Na reacts with water. Assume ideal gas nature.



$$\text{Moles of Na} = \frac{92}{23} = 4$$

$$\text{Mole of H}_2 \text{ formed} = \frac{1}{2} \times \text{Mole of Na used} = \frac{1}{2} \times 4 = 2$$

Work is done in giving out 2 mol H_2 . Thus,

$$\begin{aligned} W &= -P \times V_{\text{H}_2} = -n_{\text{H}_2} RT = -2 \times 8.314 \times 300 \\ &= -4988.4 \text{ J} \end{aligned}$$

The H_2 liberated pushes the atmospheric gas back and thus, does work in driving back the atmosphere. Note that in the case of closed vessel, $\Delta V = 0$. Therefore, $W = 0$.

CONCEPT APPLICATION EXERCISE 6.1

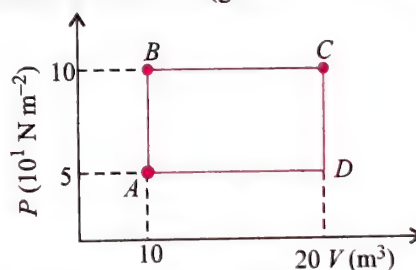
Subjective Type

- Calculate ΔU , internal energy change of a system, if it absorbs 25 kJ of heat and does 5 kJ of work.
- In a certain process, 400 J of work is done on a system which gives off 200 J of heat. What is ΔU for the process?
- During a process, a system absorbs 710 J of heat and does work. The change in ΔU for the process is 460 J. What is the work done by the system?

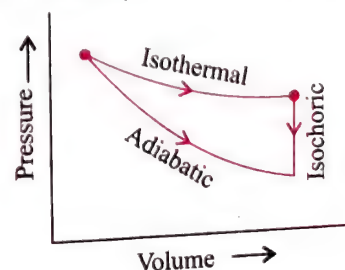
- During a process, the internal energy of the system increases by 240 kJ while the system performed 90 kJ of work on its surroundings. How much heat was transferred between the system and the surroundings during this process. In which direction did the heat flow?
- Three moles of an ideal gas are expanded isothermally and reversibly at 27°C to twice its original volume. Calculate q , w , and ΔU .
- State whether each of the following will increase or decrease the total energy content of the system:
 - Heat transferred to the surroundings
 - Work done on the system.
 - Work done by the system.
- Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one-half of its volume by an external pressure of 4 atm. Calculate q , w , and ΔU .

Objective Type

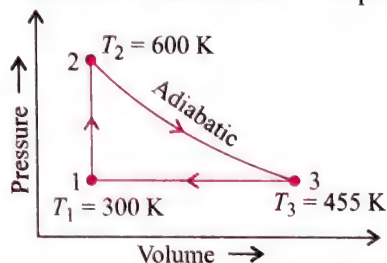
- Adiabatic expansion of an ideal gas is accompanied by
 - Increase in temperature
 - Decrease in ΔS
 - Decrease in ΔU
 - No change in any one of the above properties
- For a cyclic process, which of the following is true?
 - $\Delta S = 0$
 - $\Delta U = 0$
 - $\Delta H = 0$
 - $\Delta G = 0$
- One mole of a gas is heated at constant pressure to raise its temperature by 1°C . The work done in joules is
 - 4.3
 - 8.314
 - 16.62
 - Unpredictable
- A sample of 2 kg of helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC . Then the temperature of the states A and B are (given $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$)



- $T_A = 220.5 \text{ K}, T_B = 220.5 \text{ K}$
 - $T_A = 241 \text{ K}, T_B = 241 \text{ K}$
 - $T_A = 120.5 \text{ K}, T_B = 241 \text{ K}$
 - $T_A = 240 \text{ K}, T_B = 480 \text{ K}$
- An ideal diatomic gas is caused to pass through a cycle shown on the P - V diagram in figure, where $V_2 = 3.00V_1$. If P_1 , V_1 , and T_1 specify the state 1, then the temperature of the state 3 is
 - $(T_1/3)^1$
 - $(T_1/3)^4$
 - $(T_1/3)^{0.4}$
 - $(T_1/3)^2$

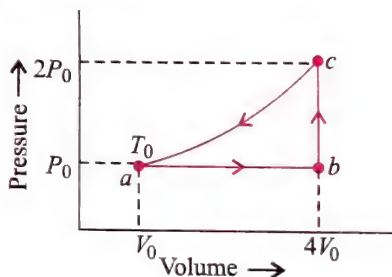


13. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in the figure below. Process 1 \rightarrow 2 takes place at constant volume, process 2 \rightarrow 3 is adiabatic and process 3 \rightarrow 1 takes place at constant pressure. Then the amount of heat added in the process 1 \rightarrow 2 is



- (1) 3740 J (2) -3740 J (3) 2810 J (4) 3228 J

14. One mole of an ideal mono-atomic gas is caused to go through the cycle shown in the figure below. Then the change in the internal energy in expanding the gas from a to c along the path abc is:



- (1) $13P_0V_0$ (2) $16RT_0$ (3) $14.5RT_0$ (4) $10.5RT_0$

ANSWERS

Subjective Type

1. 10 kJ 2. 200 J 3. -250 J 4. 330 kJ
5. 5187 J 6. a. Decrease b. Increases c. Decreases
7. $\Delta U = 0$ $q = -4984$ J $w = 4984$ J

Objective Type

8. (3) 9. (2, 3) 10. (2) 11. (3)
12. (3) 13. (1) 14. (4)

6.3 ZEROth LAW OF THERMODYNAMICS

Zeroth law of thermodynamics, also known as the law of thermal equilibrium, was put forward much after the establishment of the first and second laws of thermodynamics. It is placed before the first and second laws as it provides a logical basis for the concept of temperature of a system.

The law states as follows:

If two bodies (say A and B) are in thermal equilibrium with another body C, then the bodies A and B will also be in thermal equilibrium with each other.

Recording of temperature of a system by a thermometer is also based on this law. When a thermometer is placed in the system, it comes to thermal equilibrium with the latter and thus records a constant value.

'perfect', thermal insulator

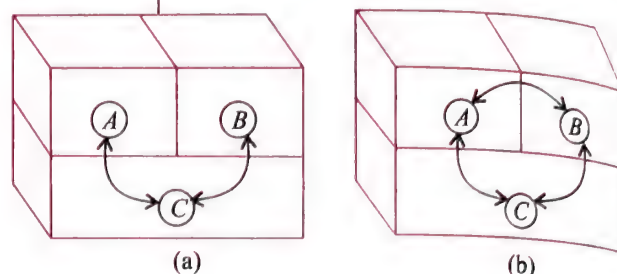


Fig 6.7 Zeroth law of thermodynamics. If A and B are in thermal equilibrium with (C) (a), they are thermal equilibrium with each other (b)

The zeroth law can be summarised in followings ways:

- Two objects at different temperature in thermal contact with each other tend to move towards the same temperature.
- Two objects in thermal equilibrium with the third one are in thermal equilibrium with each other (see Fig. 6.7).

6.4 FIRST LAW OF THERMODYNAMICS

It is our common experience that energy cannot be generated without consuming energy of some other kind. If a certain amount of one kind of energy is produced, an equal amount of some other kind of energy is consumed so that the total energy in the universe remains constant. This observation forms the basis of the *first law of thermodynamics* which is also known as the *law of conservation of energy*. It was put forward by *Robert Mayer* and *Holmholz*.

The law states that:

Energy can neither be created nor destroyed although it may be changed from one form to another.

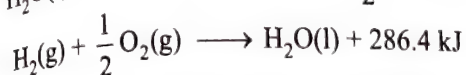
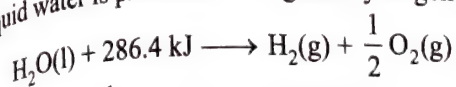
From this statement, it follows that total energy of the universe, i.e., energy of system and surroundings taken together is always constant during any physical and chemical process.

6.4.1 JUSTIFICATION FOR THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics has no theoretical proof. It is a law based on human experience and has not yet been violated. The following observations justify the validity of this law:

- It is not possible to construct a perpetual machine which can do work without the expenditure of energy. If the law were not true, it would have been possible to construct such a machine.
- James Joule (1850) conducted a large number of experiments regarding the conversion of work into heat energy. He concluded that for every 4.183 J of work done on the system, one calorie of heat is produced. He also pointed out that the same amount of work done always produces same amount of heat irrespective of how the work is done.
- Energy is conserved in chemical reactions also. For example, the electrical energy, equivalent to $286.4 \text{ kJ mol}^{-1}$ of energy is consumed when one mole of water decomposes into gaseous hydrogen and oxygen. On the other hand, the same amount

of energy in the form of heat is liberated when one mole of liquid water is produced from gases hydrogen and oxygen.



These examples justify that energy is always conserved, though it may change its form.

6.4.2 MATHEMATICAL EXPRESSION OF THE FIRST LAW OF THERMODYNAMICS

According to the first law of thermodynamics, the energy can neither be created nor destroyed. The internal energy of the system can be changed into two ways:

- By allowing heat to flow into the system or out of the system.
- by work done on the system or work done by the system.

Let us consider a system whose internal energy is U_1 . Now, if the system is supplied q amount of heat, then the internal energy of the system increases and becomes $U_1 + q$. Now, if work (w) is done on the system, then its internal energy further increases and becomes U_2 . Then, energy U_2 is the energy in the final state. It will be given as:

$$U_2 = U_1 + q + w$$

$$\text{or } U_2 - U_1 = q + w$$

$$\text{or } \Delta U = q + w$$

i.e., *Change in internal energy = Heat added to the system + Work done on the system*

The relationship between internal energy, work, and heat is a mathematical statement of the first law of thermodynamics.

6.4.3 CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS

$$\Delta U = q + w$$

- When a system undergoes a change, $\Delta U = 0$, i.e., there is no increase or decrease in the internal energy of the system, the first law of thermodynamics reduces to

$$0 = q + w$$

$$\text{or } q = -w$$

(heat absorbed from surrounding = work done by the system)

$$\text{or } w = -q$$

(heat given to surroundings = work done on the system)

- If no work is done, $w = 0$ and the first law reduces to

$$\Delta U = q$$

i.e., increase in internal of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to the heat lost by the system.

- If there is no exchange of heat between the system and surroundings (adiabatic change) $q = 0$, the first law reduces to

$$\Delta U = w_{\text{adi}}$$

It shows if work is done on the system, its internal energy will increase or if work is done by the system its internal

energy will decrease. This occurs in an adiabatic process.

- In case of gaseous system, if a gas expands against the constant external pressure, P , let the volume change be ΔV . The mechanical work done by the gas is equal to $-P \times \Delta V$.

Substituting this value in $\Delta U = q + w$,

$$\Delta U = q - P \Delta V$$

When $\Delta V = 0$,

$$\Delta U = q \text{ or } q_v$$

The symbol q_v indicates the heat change at constant volume.

Thus, the change in internal energy is equal to heat absorbed or evolved at constant temperature and constant volume.

ΔU is a state function but q and w are path functions

$\Delta U = q + w$ is a state function

Consider a system with internal energy U_i in the initial state A . The conditions of temperature and pressure changed following path I so that the system acquires the final state B with internal energy U_f . Now if the system is returned to state A following path II, then the energy involved in path I and path II is equal in magnitude. If energy change in path I and path II not equal, assuming energy change in path I > energy change in path II, then by carrying out the process from $A \rightarrow B$ by path I and from $B \rightarrow A$ by path II, some energy could be created inspite of the fact that original state A has been restored. This is contrary to the first law of thermodynamics. Hence, the energy change in going from $A \rightarrow B$ by path I or by path II must be same. In other words, ΔU is independent of path and is thus a state function (Fig. 6.8):

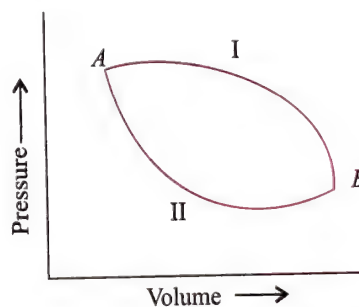
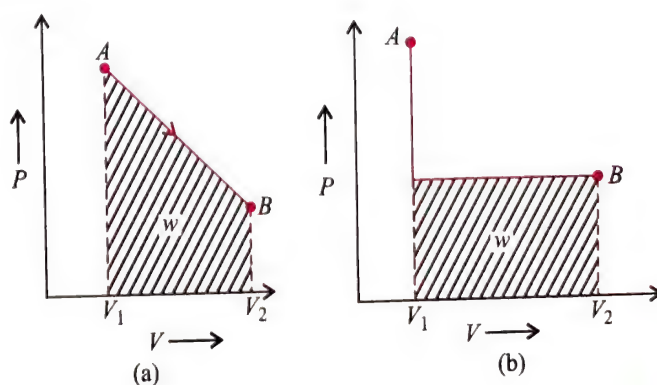


Fig. 6.8 P-V work showing ΔU is a state function

q and w are path functions

Let us consider the system to be changed from initial state A to final state B by three different paths as shown in Fig. (6.9a-c) given below:



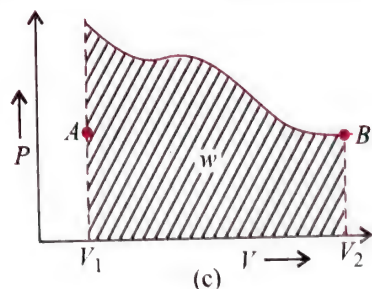


Fig. 6.9

The work done (w) during the process is given by the shaded area in all the P - V diagrams. It is represented by the shaded portion of the diagram. It is clear from the diagram that the shaded areas are different. In other words, magnitude of w is different in different paths. Heat (q) is given by the expression $\Delta U = q - w$. ΔU being state function is same in different paths, but w is different. Consequently, $(\Delta U - w)$, i.e., q , will also be different. In other words, both q and w are path dependent but ΔU ($q + w$) is path independent, i.e., state function.

- Note:**
1. Both work and heat appear only during a change of state.
 2. q is +ve when system absorbs heat and -ve when system evolves heat.
 3. W is +ve when work is done on the system and -ve when system performs a work.
 4. Work, energy and heat have same units whereas energy is a thermodynamic property of the system, work and heat are not.
 5. It should be noted that the work done during the isothermal reversible process is greater than adiabatic process.
 6. $1 \text{ cal} > 1 \text{ joule} > 1 \text{ erg}$.
 7. Both work and heat appear only at the boundary of the system.
 8. Theoretically, work can be fully converted into heat, but heat cannot be fully converted into work.

QUESTIONS BASED ON FIRST LAW OF THERMODYNAMICS

ILLUSTRATION 6.17

A system is provided 50 J of heat and work done on the system is 20 J. What is the change in the internal energy?

Sol. $q = 50 \text{ J}$
 $w = +20 \text{ J}$ (work done on the system)
 $\therefore \Delta U = q + w = 50 + 20 = 70 \text{ J}$

ILLUSTRATION 6.18

The work done by a system is 10 J, when 40 J heat is supplied to it. Calculate the increase in the internal energy of system.

Sol. $W = -10 \text{ J}; \quad q = 40 \text{ J}$
 From the first law, $\Delta U = q + w = 40 - 10 = 30 \text{ J}$

ILLUSTRATION 6.19

A gas occupies 2 L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm. Calculate the change in its internal energy.

Sol. Work done $= -P \times \Delta V = 1 \times (2.5 - 2.0)$
 $= -0.5 \text{ L atm}$

Therefore, work is carried out at constant P and thus irreversible.

$$= -\frac{0.5 \times 1.987 \times 4.184}{0.0821} \text{ J} = 0.5 \times 101.328 \text{ J}$$

$$= -50.631 \text{ J}$$

From the first law of thermodynamics,

$$\therefore q = \Delta U - w$$

$$300 = \Delta U + 50.63 \therefore \Delta U = 249.37 \text{ J}$$

ILLUSTRATION 6.20

A certain electric motor produced 16 kJ of energy each second as mechanical work and lost 3 kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each second?

Sol. Energy is lost from the system as work, thus W is negative.
 $\therefore w = -16 \text{ kJ}$

Energy is lost as heat, so $q = -3 \text{ kJ}$

Therefore, by the first law of thermodynamics,

$$\Delta U = q + w = -3 - 16 = -19 \text{ kJ}$$

ILLUSTRATION 6.21

An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T . The other portion is a perfect vacuum. If a hole is opened between the two portions, calculate

- a. the change in internal energy.
- b. the change in temperature.

Sol. The system being thermally insulated, $q = 0$. The gas expands through the hole in other portion to show free expansion, i.e.,

$$w = -\int P \Delta V = 0 \quad (\text{Since, } P = 0)$$

Also from the first law of thermodynamics,

$$q = \Delta U + w$$

Since, $q = 0, w = 0$

Also internal energy $U = \frac{3}{2} RT$. Since, the internal energy remains same ($\therefore \Delta U = 0$), thus the temperature will also remain constant. ($\therefore \Delta U = 0$)

ILLUSTRATION 6.22

2.8 g of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate ΔU , q , and W for the gas.

Illustration 6.22 Initially for N_2 , using gas equation $PV = nRT$

$$20 \times V_1 = \frac{2.8}{28} \times 0.0821 \times 300 \Rightarrow V_1 = 0.123 \text{ L}$$

Finally for N_2

$$1 \times V_2 = \frac{2.8}{28} \times 0.0821 \times 300 \Rightarrow V_2 = 2.463 \text{ L}$$

$$W = -P \times \Delta V \quad [\because \text{work is done against constant } P, \text{ therefore, irreversible}]$$

$$= -1 \times (2.463 - 0.123) \text{ L atm}$$

$$= -2.340 \text{ L atm}$$

$$= -\frac{2.340 \times 1.987}{0.0821} \text{ cal} = -\frac{2.340 \times 1.987 \times 4.184}{0.0821} \text{ J}$$

$$W = -236.95 \text{ J}$$

$$\text{Now } q = \Delta U - W$$

$$q = 0 + 236.95 = 236.95 \text{ J}$$

($\because \Delta U = 0$ for isothermal process)

ILLUSTRATION 6.23

At 27°C , one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 20 atm to 100 atm. Calculate ΔU and q . ($R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$)

Sol. $W = 2.303nRT \log \frac{P_1}{P_2}$

$$W = 2.303 \times 1 \times 2 \times 300 \log \frac{20}{100} = -965.84 \text{ cal}$$

$$\text{For isothermal change, } \Delta U = 0$$

$$\text{Also } q = \Delta U - W = 0 + 965.84 \text{ cal}$$

$$\therefore q = +965.84 \text{ cal}$$

ILLUSTRATION 6.24

One mole of an ideal gas is heated at constant pressure from 0°C to 100°C .

a. Calculate the work done.

b. If the gas were expanded isothermally and reversibly at 0°C from 1 atm to some other pressure P_r , what must be the final pressure if the maximum work is equal to the work in (a)?

Sol. a. Work involved in heating of gas

$$W_a = -P \Delta V = -P(V_2 - V_1)$$

$$= -P \left(\frac{nRT_2}{P} - \frac{nRT_1}{P} \right) = -nR(T_2 - T_1)$$

$$= -1 \times 8.314 (373 - 273) = -831.4 \text{ J}$$

b. Now the work equivalent to 831.4 cal is used up in causing reversible isothermal expansion of gas at 0°C , then

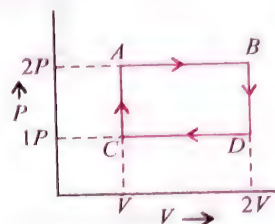
$$W_R = -2.303nRT \log_{10} \frac{P_1}{P_2}$$

$$-831.4 = -2.303 \times 1 \times 8.314 \times 273 \log_{10} \frac{P_1}{P_2}$$

$$\therefore P_1 = 0.694 \text{ atm}$$

ILLUSTRATION 6.25

An ideal mono-atomic gas follows the path $ABDC$. The work done during the complete cycle is



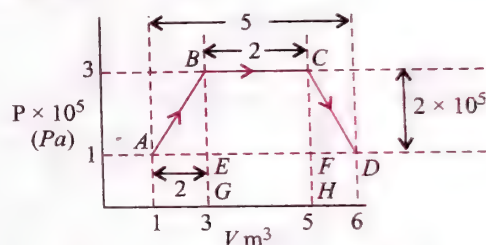
- a. $-PV$ b. $-2PV$ c. $-\frac{1}{2}PV$ d. Zero

Sol. a. Net work done during the complete cycle is equal to area under the cycle ($-ve$ if the cycle is clockwise, i.e., work done by the gas and $+ve$ when cycle is anticlockwise, i.e., work done on the gas)

$$w = -P \times V = -(2P - P) \times (2V - V) = -PV$$

ILLUSTRATION 6.26

The net work done through a series of changes reported in figure for an ideal gas is



- a. $-6 \times 10^5 \text{ J}$ b. $-7 \times 10^5 \text{ J}$
c. $-12 \times 10^5 \text{ J}$ d. $+12 \times 10^5 \text{ J}$

Sol. b. Area of trapezium

$$= \frac{1}{2} \times h \times \text{sum of parallel sides}$$

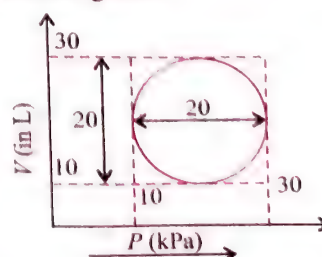
$$= \frac{1}{2} \times 2 \times 10^5 \times (2 + 5)$$

$$= 7 \times 10^5$$

$$\text{Net work done} = -7 \times 10^5 \text{ J}$$

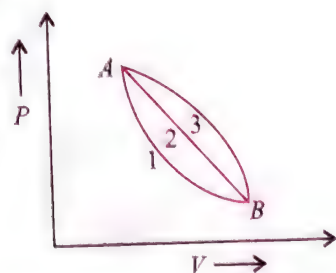
ILLUSTRATION 6.27

I. Heat energy absorbed by a system in going through a cyclic process shown in figure is



- a. $10^7 \pi \text{ J}$ b. $10^4 \pi \text{ J}$ c. $10^2 \pi \text{ J}$ d. $10^{-3} \pi \text{ J}$

- II. A given mass of gas expands from state A to state B by three paths 1, 2, and 3 as shown in the figure below. If w_1 , w_2 and w_3 respectively, be the work done by the gas along three paths, then



- a. $w_1 > w_2 > w_3$
 b. $w_1 < w_2 < w_3$
 c. $w_1 = w_2 = w_3$
 d. $w_1 < w_2$; $w_1 < w_3$

Sol.

- I. c. Work done = Area of sphere

$$= \pi r^2 = \pi \times 10^2 \Rightarrow \left(r = \frac{1}{2} (30 - 10) = 10 \right)$$

- II. b. Work is equal to area under $P - V$ graph (when P is plotted along y-axis). As area under graph 3 is maximum and area under graph 1 is minimum, so W_3 is maximum and W_1 is minimum

$$\therefore W_1 < W_2 < W_3$$

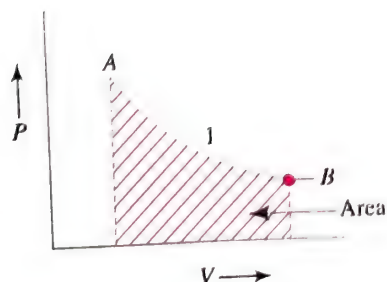
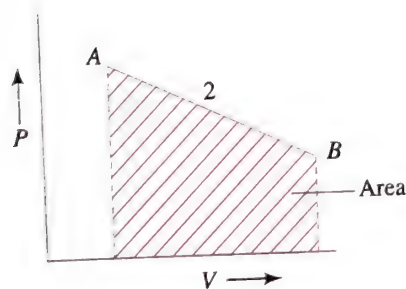
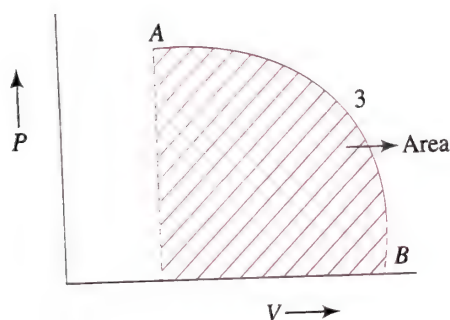


ILLUSTRATION 6.28

- I. Can we measure the absolute value of internal energy?

- II. One mole of SO_2 at 298 K and 1 atm pressure is heated in a closed vessel so that its temperature is 475 K and pressure is 4 atm. It is then cooled so that temperature becomes 298 K and pressure is 1 atm. What is the change in the internal energy of the gas?

- III. Neither q nor w is a state function but $q + w$ is a state function. Explain why?

- IV. Which of the following are state functions?

- a. q
 b. Heat capacity
 c. Specific heat capacity
 d. ΔH
 e. w

- V. Under what conditions is the heat of reaction equal to enthalpy change?

- a. $\Delta H = q_p$
 b. $\Delta H = q_v$
 c. $\Delta H > q_p$
 d. $\Delta H < q_p$

Sol.

- I. No, because the internal energy is the sum of different types of energies, some of which cannot be determined.

- II. No change in the internal energy because it is a state function.

- III. $q + w$ is equal to ΔU which is a state function.

- IV. d.

- V. a. The heat of reaction is equal to enthalpy change at constant pressure, i.e., $\Delta H = q_p$.

ILLUSTRATION 6.29

A gas expands from 3 dm³ to 5 dm³ against a constant pressure of 3 atm. The work done during the expansion is used to heat 10 mol of water at temperature 290 K. Find the final temperature of water, if the specific heat of water = 4.18 J g⁻¹ K⁻¹.

Sol. Work done = $-P \Delta V$

$$= -(3 \times 2) \text{ L-atm}$$

$$= -6 \times 101.3 \text{ J}$$

$$= -607.8 \text{ J}$$

$$(\because 1 \text{ L-atm} = 101.3 \text{ J})$$

$$\text{Heat lost} = \text{Heat gained by H}_2\text{O (ms } \Delta t)$$

$$607.8 \text{ J} = 180 \times 4.18 \times \Delta T$$

$$\Delta T = \frac{607.8}{10 \times 18 \times 4.18} = 0.808 \text{ K}$$

$$\Rightarrow T_f = 290 + 0.808 = 290.808 \text{ K}$$

ILLUSTRATION 6.30

Classify the following as open, closed, or isolated system:

- a. A beaker containing as open, boiling water.
 b. A chemical reaction taking place in an enclosed flask.
 c. A cup of tea placed on a table.
 d. Hot water placed in perfectly insulated closed container.
 e. A thermos flask containing hot coffee.

Sol. Types of system:

- a. Open system
 b. Closed system
 c. Open system
 d. Isolated system
 e. Isolated system

6.5 ENTHALPY (H)

We know that the heat absorbed at constant volume is equal to the change in the internal energy, i.e., $\Delta U = q_V$. But most of the chemical reactions are carried out not at constant volume but in open flasks or test tubes under constant atmospheric pressure, therefore such reactions may involve change in volume. The energy change occurring involve change in volume. The energy change occurring during such reactions may not be equal to the internal energy change but also include energy change due to expansion or contraction against the atmospheric pressure. In order to study the heat changes of chemical reactions at constant temperature and pressure, a new function *enthalpy* is introduced. Enthalpy may be defined as the sum of the internal energy and the pressure-volume energy of the system.

Mathematically, it may be put as $H = U + PV$

6.5.1 IMPORTANT FEATURES OF ENTHALPY

- It is a state function and is an extensive property.
- It is also called heat content of the system.
- Its value depends upon amount of the substance, chemical nature of the substance, and conditions of temperature and pressure.

It is not possible to determine the absolute value of enthalpy of a system because the absolute value of internal energy (U) is not known. However, change in enthalpy (ΔH) taking place during the process can be experimentally determined. Change in enthalpy is equal to the difference between the enthalpies of products (ΣH_P) and reactants (ΣH_R).

Thus, change in enthalpy can be expressed as:

$$\Delta H = \Sigma H_P - \Sigma H_R$$

6.5.2 ENTHALPY CHANGE (ΔH)

Let us consider a chemical reaction, $A \longrightarrow B$, under a given set of conditions, the change in enthalpy may be expressed as

$$\Delta H = H_B - H_A$$

where H_A is the enthalpy in state A and H_B is the enthalpy in state B and ΔH is the enthalpy change. It may be noted that like internal energy, enthalpy is also a function of the state of the system and, therefore, ΔH is independent of the manner in which the final state achieved.

Change in enthalpy, (ΔH) may be expressed as

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + P \Delta V + V \Delta P$$

If the process is carried out at constant pressure i.e., $\Delta P = 0$, then

$$\Delta H = \Delta U + P \Delta V$$

$$\text{Now, } \Delta U = q + w$$

If work done during the change is only expansion work,

$$w = -P \Delta V \text{ so that}$$

$$\Delta U = q - P \Delta V$$

Substituting in equation (i), the value of ΔU , we get

$$\Delta H = q - P \Delta V + P \Delta V = q$$

$$\therefore \Delta H = q_P \quad (\text{at constant pressure})$$

where q_P indicates that heat change has taken place at constant pressure. Thus,

The enthalpy change is a measure of heat change (evolved or absorbed) taking place during a process at constant pressure. It is a state function and an extensive property as its value depends on the quantity of the system.

Thus, we can sum up:

If q is the amount of heat absorbed by the system.

$$q \text{ (at constant volume)} = \Delta U$$

$$q \text{ (at constant pressure)} = \Delta H$$

Relationship Between ΔH and ΔU

As already studied, ΔH and ΔU are related as

$$\Delta H = \Delta U + P \Delta V \quad \dots(i)$$

The difference between ΔH and ΔU is not usually significant for solids and liquids. However, when the systems involve gases, the difference becomes significant. Consider a chemical reaction taking place at a constant temperature (T) and pressure (P). Let V_r is the total volume of the gaseous reactants and V_p is the total volume of the gaseous products, n_r is the number of moles of gaseous reactants, and n_p is the number of moles of gaseous products. According to the ideal gas equation:

$$PV = nRT$$

$$\text{For reactants, } PV_r = n_r RT \text{ (at constant } T \text{ and } P) \quad \dots(ii)$$

$$\text{For products, } PV_p = n_p RT \text{ (at constant } T \text{ and } P) \quad \dots(iii)$$

Subtracting equation (2) from equation (3), we get

$$P(V_p - V_r) = n_p RT - n_r RT = (n_p - n_r) RT$$

$$\text{or } P \Delta V = \Delta n_g RT \quad \dots(iv)$$

where Δn_g is the change in the number of gaseous moles of product and gaseous moles of reactants.

Thus, equation (i) becomes

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\left[\begin{array}{c} \text{Energy} \\ \text{change at} \\ \text{constant } P \end{array} \right] = \left[\begin{array}{c} \text{Energy change} \\ \text{at constant } V \end{array} \right] + \left[\begin{array}{c} \text{Change in the} \\ \text{number of} \\ \text{gaseous moles} \end{array} \right] \times RT$$

This relation is very useful for converting ΔH into ΔU or ΔU into ΔH .

$$\text{Thus, } \Delta H = \Delta U + P \Delta V$$

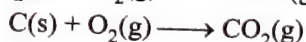
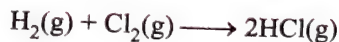
$$\Delta H = \Delta U + \Delta n_g RT$$

It is important to note that ΔH will be equal to ΔU under the following conditions:

- Reactions that do not involve any gaseous components. For example, reaction between aqueous solution of hydrochloric acid and sodium hydroxide.

$$\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$
- Reactions carried out in closed vessels of fixed volume i.e., $\Delta V = 0$.
- Reactions that involve gaseous reactants and products but there is no change in the number of moles of the gaseous components.

For example,

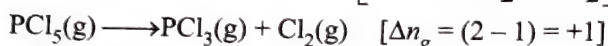
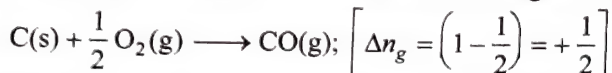


In all such reactions, the volume change is zero, i.e., $\Delta n_g = 0$.

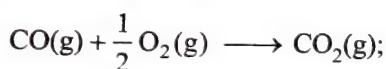
$$\therefore \Delta H = \Delta U + \Delta n_g RT = \Delta U + 0 \times RT = \Delta U$$

However, in gaseous reactions having Δn_g not equal to zero, ΔH and ΔU will be different. For example:

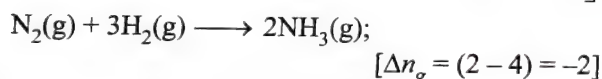
- a. Reactions in which there is an increase in the number of moles of the gaseous components.** In such cases, Δn_g is positive and consequently, the enthalpy change (ΔH) is greater than the internal energy change (ΔU), i.e., $\Delta H > \Delta U$. Some examples of such reactions are given below:



- b. Reactions in which there is a decrease in the number of moles of the gaseous components.** In such cases, Δn_g is negative and consequently, the enthalpy change (ΔH) is less than the internal energy change (ΔU) i.e., $\Delta H < \Delta U$. Some examples of such reactions are given below:



$$\left[\Delta n_g = \left(1 - 1\frac{1}{2} \right) = -\frac{1}{2} \right]$$



Thus, for gaseous reactions, the difference between ΔH and ΔU depends upon the value of Δn_g . For example,

$$\Delta n_g = 0; \Delta H = \Delta U$$

$$\Delta n_g = -ve; \Delta H < \Delta U$$

$$\Delta n_g = +ve; \Delta H > \Delta U$$

Note: 1. The change in enthalpy, $\Delta H = \Delta U + P\Delta V$. Also

$$\Delta H = \Delta U + \Delta n_g RT$$

- When $\Delta n_g = 0$; then $\Delta H = \Delta U$
 - If $\Delta n_g > 0$, then $\Delta H > \Delta U$ and similarly if $\Delta n_g < 0$ then $\Delta H < \Delta U$
- Enthalpy also changes when a substance undergoes phase transition.
 - For reactions involving solids and liquids only, $\Delta H = \Delta U$.
 - For a reaction involving solid, liquid and gases, the value Δn is evaluated by the difference in number of moles of gaseous reactants and products.
 - Enthalpy change (ΔH) is calculated using calorimeter (an open vessel)

$$\Delta H = C \times \Delta T \times \frac{M_w}{m}$$

where C = heat capacity of calorimeter system,
 ΔT = change in temperature,

M_w = molecular mass of the substance, and
 m = amount of the substance.

This method is not suitable for

- reactions which are extremely slow.
- reactions which are accompanied by very small enthalpy change.
- reactions which do not go to completion.

QUESTIONS BASED ON ENTHALPY (ΔH) AND INTERNAL ENERGY (ΔU)

ILLUSTRATION 6.31

If ΔH is the enthalpy change and ΔU the change in internal energy accompanying a gaseous reaction, then

- ΔH is always less than ΔU .
- ΔH is always greater than ΔU .
- ΔH is less than ΔU if the number of moles of gaseous products is greater than the number of moles of gaseous reactants.
- ΔH is less than ΔU if the number of moles of gaseous products is less than the number of moles of gaseous reactants.

Sol. d. As $\Delta H = \Delta U + \Delta n_g RT$

ΔH value is less than or greater than ΔU depending on the value of Δn_g which is the change in number of moles of the gaseous components.

As result, (a) and (b) cannot be true.

$\Delta H < \Delta U$ when $\Delta n_g < 0$, hence (c) is also false only (d) is correct.

Hence, (d) is the correct answer.

ILLUSTRATION 6.32

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol^{-1} . Calculate the internal energy change, when

- 1 mol of water is vaporized at 1 bar pressure and 100°C .
- 1 mol of water is converted into ice.

Sol.

- The change $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

$$\Delta H = \Delta U + \Delta n_g RT$$

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$$\begin{aligned} \Delta U &= 41.00 \text{ kJ mol}^{-1} - 1 \times 8.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 373 \text{ K} \\ &= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1} \\ &= 37.904 \text{ kJ mol}^{-1} \end{aligned}$$

- The change $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$

There is negligible change in volume,

So, we can put $p\Delta V = \Delta n_g RT \approx 0$ in this case,

$$\Delta H \equiv \Delta U$$

so, $\Delta U = 41.00 \text{ kJ mol}^{-1}$

ILLUSTRATION 6.33

- I. ($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is
($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
a. $-1238.78 \text{ J mol}^{-1}$ b. $1238.78 \text{ J mol}^{-1}$
c. $-2477.57 \text{ J mol}^{-1}$ d. $2477.57 \text{ J mol}^{-1}$
- II. The difference between the heats of reaction at constant pressure and a constant volume for the reaction
 $2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$ at 25°C in kJ is
a. -7.43 b. $+3.72$ c. -3.72 d. $+7.43$
- III. The latent heat of vapourisation of a liquid at 500 K and 1 atm pressure is 30 kcal mol^{-1} . What will be the change in internal energy of 3 mol of liquid at same temperature?
a. 13.0 kcal b. -13.0 kcal
c. 27.0 kcal d. -27.0 kcal
- IV. What is value of ΔU for reversible isothermal evaporation of 90 g water at 100°C ? Assuming water vapour behaves as an ideal gas, $\Delta_{\text{vap, water}} H = 540 \text{ cal g}^{-1}$
a. $9 \times 10^3 \text{ cal}$ b. $6 \times 10^3 \text{ cal}$
c. 4.49 cal d. None of the above

Sol.

- I. b. $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$
 $\Delta H - \Delta U = \Delta n_g RT$
 $= \frac{1}{2} \times 8.314 \times 298 = 1238.78 \text{ J mol}^{-1}$
- II. a. $\Delta H = \Delta U + \Delta n_g RT$. Here, $\Delta n_g = 12 - 15 = -3$.
Thus, $\Delta H - \Delta U = -3 \times 8.314 \times 10^{-3} \times 298 = -7.43 \text{ kJ}$
- III. c. $\therefore \Delta H = \Delta U + \Delta n RT$
 $\therefore \Delta H = 30 \text{ kcal}$
 $3\text{H}_2\text{O}(\text{l}) \longrightarrow 3\text{H}_2\text{O}(\text{v})$
 $\Delta n = 3 - 0 = 3$
 $\Rightarrow 30 = \Delta U + 3 \times 0.0821 \times 500 \times 10^{-3}$
 $\Delta U = 27 \text{ kcal}$
- d. Heat of system $(\Delta H)_V = m \times \Delta H$
 $= 90 \times 540 = 48600 \text{ cal}$
 $\Delta H = \Delta U + P(V_V - V_L) = \Delta U + \Delta n RT$
or $48600 = \Delta U + \frac{90}{18} \times 2 \times 373$
or $\Delta U = 48600 - 3730 = 44870 \text{ cal}$

ILLUSTRATION 6.34

- I. The enthalpy combustion of a substance
a. Is always positive

- b. Is always negative
- c. Can be either zero or greater than zero
- d. Is unpredictable till the calculations are done

- II. One litre-atmosphere is approximately equal to
a. 19.2 J b. 101.3 J c. 8.31 J d. 831 J
- III. Calorific value of fat
a. Greater than that of carbohydrate or protein
b. Less than either of carbohydrate or protein
c. Less than that of carbohydrate
d. Greater than that of carbohydrate

Sol.

- I. b. In combustion, energy releases. Hence it is exothermic, $\Delta H = -ve$.
- II. b. $1 \text{ L-atm} = 101.3 \text{ J}$
- III. a.

ILLUSTRATION 6.35

- I. X g of ethanal was subjected to combustion in a bomb calorimeter and the heat produced is Y J. Then
a. $\Delta U (\text{combustion}) = -X \text{ J}$
b. $\Delta U (\text{combustion}) = -Y \text{ J}$
c. $\Delta U (\text{combustion}) = -\frac{44Y}{X} \text{ J mol}^{-1}$
d. $\Delta H (\text{combustion}) = \frac{44Y}{X} \text{ J mol}^{-1}$

- II. The reaction



- a. Endothermic b. Exothermic
- c. $\Delta H = 0$ d. Unpredictable

- III. A hypothetical reaction, $A \rightarrow 2B$, proceeds via following sequence of steps



The heat of reaction is

- a. $q_1 - q_2 + 2q_3$ b. $q_1 + q_2 - 2q_3$
- c. $q_1 + q_2 + 2q_3$ d. $q_1 + 2q_2 - 2q_3$

Sol.

$$\text{I. c. } \therefore \text{Mole} = \frac{W}{\text{Molecular weight}}$$

$$\text{II. b. } \Delta H = \Delta U + \Delta n_g RT$$

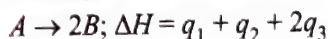
$$\text{or } \Delta H \approx \Delta n_g RT$$

$$\Delta n_g = n_p - n_R = \left(1 - \left(1 + \frac{1}{2}\right)\right) = -\frac{1}{2}$$

$$\therefore \Delta H = -ve \text{ or exothermic}$$

- III. c. $A \rightarrow C; \quad \Delta H = q_1$
 $C \rightarrow D; \quad \Delta H = q_2$
 $D \rightarrow 2B; \quad \Delta H = q_3 \times 2$

Adding all three equations, we get



6.6 HEAT CAPACITY

When heat is transferred to the system it raises the temperature of the system. The increase in temperature (ΔT) is directly proportional to the quantity of heat (q) absorbed by the system. Mathematically, it may be shown as

$$q \propto \Delta T \text{ or } q = C \cdot \Delta T \quad \dots(i)$$

where C is known as the heat capacity of the system. Its value depends upon the size, composition, and nature of the system.

Equation (i) can be written as

$$C = \frac{q}{\Delta T} \quad \dots(ii)$$

Thus, heat capacity of the system is defined as the quantity of the heat required to raise its temperature by one degree. Equation (ii) shows that a given amount of heat will raise the temperature of the system to a smaller extent if its heat capacity is large and vice-versa.

For infinitesimally small changes, if dq is the heat required to raise the temperature of the system from T to $(T + dT)$, then equation (ii) can be written as

$$C = \frac{dq}{dT}$$

Heat (q) is not a state function but depends on the path. Likewise heat capacity is also a path function. Thus, conditions such as constant volume or constant pressure have to be specified to define the path for calculating the heat capacity of a system particularly in a gaseous system.

6.6.1 HEAT CAPACITY AT CONSTANT VOLUME (C_V)

The amount of heat change of a system at constant volume i.e., change in the heat of a system with per unit rise in a temperature at constant volume ($\Delta V = 0$)

$$\therefore C_V = \left(\frac{dq_V}{dT} \right)$$

From the first law,

$$dq = dU + P dV$$

$$\text{at } dV = 0, dq = du$$

$$\text{so } C_V = \left(\frac{dU}{dT} \right)_V$$

Thus, heat capacity at constant volume represent rate of increase of internal energy of the system with temperature.

6.6.2 HEAT CAPACITY AT CONSTANT PRESSURE (C_P)

The amount of change in heat of system with per unit rise in temperature at constant pressure, is called heat capacity at constant pressure; $\Delta V \neq 0$

$$C_P = \left(\frac{dq}{dT} \right)_P$$

From the first Law

$$dq = dU + P dV$$

$$\text{Also } H = U + PV$$

$$\therefore dH = dU + P dV$$

$$dU = dH - P dV, \text{ substituting in equation (i)}$$

$$\text{or } dq = dH - P dV + P dV = dH$$

$$\therefore C_P = \left(\frac{dq}{dT} \right)_P = \left(\frac{dH}{dT} \right)_P$$

Thus, heat capacity at constant pressure represents the rate of increase of enthalpy of system with temperature.

Relation Between C_P and C_V

Since, enthalpy of the system is defined as

$$H = U + PV$$

From ideal gas equation,

$$PV = nRT$$

where $n = 1$

$$PV = RT$$

$$\text{or } H = U + RT$$

On differentiating with respect to T

$$\therefore \frac{dH}{dT} = \frac{dU}{dT} + R$$

$$\text{or } C_P = C_V + R$$

$$\text{or } (C_P - C_V) = R = 1.99 \text{ cal K}^{-1} \text{ mol}^{-1} \\ = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

The difference between C_P and C_V is equal to the work done by 1 mol of a gas in expansion when heated through 1°C .

C_P is Always Greater than C_V

- When gas is heated at constant volume, the pressure of a gas has to increase. As the gas is not allowed to expand, therefore in case of C_V heat is required for raising the temperature of one mole of a gas through one degree.
- When gas is heated at constant P , it expands. The gas has done some work against external pressure. More heat is, therefore, supplied to raise its temperature through one degree.
 - Thus, C_P is heat required for the purpose of
 - Increasing temperatures of one mole of gas through one degree.
 - For increasing the volume of the gas against external pressure.

$$C_P > C_V$$

C_P/C_V Ratio

The ratio of molar heat capacities at constant pressure to that at constant volume is represented by γ . The value of γ gives information about the atomicity of gases.

$$\frac{C_P}{C_V} = \gamma$$

6.6.3 MOLAR HEAT CAPACITY

The molar heat capacity of a substance (C_m) is the heat required to raise the temperature of 1 mol of the system through one degree. If C is the heat capacity of n mol of the system, then its molar heat capacity C_m is given by $C_m = C/n$.

For gaseous system, the heat capacities of 1 mol of a gas at constant volume and at constant pressure are called molar heat capacities. These are represented by C_V and C_P , respectively. It is an intensive property.

6.6.4 SPECIFIC HEAT CAPACITY

This term is used more frequently for solids and liquids. The specific heat capacity (or specific heat) of a substance is defined as the amount of heat required to raise the temperature of 1 g of the substance through one degree.

$$\text{Specific heat capacity (C)} = \frac{\text{Heat capacity}}{\text{Mass}} = \frac{C}{m}$$

$$\text{or } C = \frac{q}{m \Delta T}$$

$$\text{or } q = C \times m \times \Delta T$$

Units of specific heat capacity are: $\text{J g}^{-1} \text{K}^{-1}$ or $\text{J g}^{-1} ^\circ\text{C}^{-1}$

Note:

1. Since molar heat capacities of solids are approximately equal to one another, i.e., ΔC_P or $\Delta C_V = 0$. Therefore, ΔH of reactions involving only solids do not change appreciably with temperature.

$$C_P/C_V = \gamma$$

2. The value of γ depends upon the atomicity of gaseous molecules. Thus

$\gamma = 1.66$, for monoatomic gases (e.g., He, Ne, Ar etc.)

$\gamma = 1.40$ for diatomic gases (e.g., O_2 , H_2 , N_2 , Cl_2 etc.)

$\gamma = 1.33$, for triatomic gases (e.g., SO_2 , O_3 , CO_2 etc.)

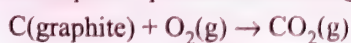
3. Dulong and Petit law. The product of specific heat and molar mass of any metallic element is equal to $6.4 \text{ cal/mole } ^\circ\text{C}$. i.e., Specific heat \times Molar mass = 6.4

This law is applicable to solid elements only, exception being Be, B, C and Si.

QUESTION BASED ON HEAT CAPACITY

ILLUSTRATION 6.36

1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation



During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K , what is the enthalpy change for the above reaction at 298 K and 1 atm?

Sol. Suppose q is the quantity of heat from the reaction mixture and C_V is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$$q = C_V \times \Delta T$$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$\begin{aligned} q &= -C_V \times \Delta T = -20.7 \text{ kJ/K} \times (299 - 298) \text{ K} \\ &= -20.7 \text{ kJ} \end{aligned}$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1 g of graphite = -20.7 kJ K^{-1}

For combustion of 1 mol of graphite,

$$\begin{aligned} &= \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}} \\ &= -2.48 \times 10^2 \text{ kJ mol}^{-1}, \quad (\text{Since } \Delta n_g = 0.) \\ \Delta H = \Delta U &= -2.48 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.37

A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K? Calculate the internal energy of vaporisation at 100°C .

$$\Delta_{\text{vap}} H^\ominus \text{ for water at } 373 \text{ K} = 40.66 \text{ kJ mol}^{-1}$$

Sol. The process of evaporation is



Number of moles in 18 g $\text{H}_2\text{O(l)}$ is

$$= \frac{18 \text{ g}}{18 \text{ g mol}^{-1}} = 1 \text{ mol}$$

$$\Delta_{\text{vap}} U = \Delta_{\text{vap}} H^\ominus - p\Delta V = \Delta_{\text{vap}} H^\ominus - \Delta n_g RT$$

(assuming steam behaving as an ideal gas)

$$\begin{aligned} \Delta_{\text{vap}} H^\ominus - \Delta n_g RT &= 40.66 \text{ kJ mol}^{-1} - (1)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373 \text{ K})(10^{-3} \text{ kJ}) \\ \Delta_{\text{vap}} U^\ominus &= 40.66 \text{ kJ mol}^{-1} - 3.10 \text{ kJ mol}^{-1} \\ &= 37.56 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.38

A sample of oxygen gas expands its volume from 3 to 5 L against a constant pressure of 3 atm. If the work done during expansion be used to heat 10 mol of water initially present at 290 K, its final temperature will be

(specific heat capacity of water = $4.18 \text{ J K}^{-1} \text{ g}^{-1}$)

- a. 292.0 K b. 290.9 K c. 298.0 K d. 293.7 K

Sol. b. Work done in expansion

$$= P \times V = 3 \times (5 - 3) = 6 \text{ L-atm}$$

$$\text{We have } 1 \text{ L-atm} = 101.3 \text{ J}$$

$$\text{Work done} = 6 \times 101.3 \text{ J} = 607.8 \text{ J}$$

Let ΔT be the change in temperature of water.

$$\therefore P \Delta V = m \times s \times \Delta T$$

$$607.8 = 180 \times 4.184 \times \Delta T$$

$$\Delta T = 0.81 \text{ K}$$

$$T_f = T_i + \Delta T = 290.9 \text{ K}$$

$$\left(\begin{array}{l} m = \text{mol} \times Mw \\ = 10 \times 18 = 180 \end{array} \right)$$

ILLUSTRATION 6.39

I. The magnitude of enthalpy changes for reversible adiabatic expansion of a gas from volume V_1 to V_2 (in L) is ΔH_1 and for irreversible adiabatic expansion for the same expansion is ΔH_2 . Then

a. $\Delta H_1 > \Delta H_2$

b. $\Delta H_1 < \Delta H_2$

c. $\Delta H_1 = \Delta H_2$

d. $\Delta H_1 = \Delta U_1$ and $\Delta H_2 = \Delta U_2$

where ΔU_1 and ΔU_2 are the changes in magnitudes for the internal energy of gas in the two expansions.

II. The molar heat capacity for a gas at constant T and P is

a. $\frac{3}{2} R$

b. $\frac{5}{2} R$

c. Dependent on the atomicity of the gas

d. Infinity

III. A system has internal energy equal to U_1 , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be

a. $(U_1 + 150)$

b. $(U + 1050)$

c. $(U_1 - 150)$

d. None of these

Sol.

I. We know that work done in a reversible expansion process is always greater than in an irreversible expansion process

Using the first law of thermodynamics, $q = 0 = \Delta U + (-w)$

Thus, decrease in U will be larger in reversible adiabatic than irreversible adiabatic expansion and since $\Delta U = nC_V \Delta T$, we can conclude that ΔT in reversible adiabatic expansion will be greater than in irreversible adiabatic expansion.

Now, $\Delta H_1 = nC_P \Delta T_1$, and $\Delta H_2 = nC_P \Delta T_2 \Rightarrow \Delta H_1 > \Delta H_2$

II. d. $C_P = \left(\frac{dH}{dT} \right)_P$ Since at constant T , $dT = 0$

$$\therefore C_P = \infty$$

III. a. Initial internal energy = U_1

Heat taken out = -450 J

Work done on the system = 600 J

$$\therefore \text{Internal energy} = q + w$$

$$= -450 + 600 = 150 \text{ J}$$

$$\therefore \text{Total energy} = [U_1 + 150]$$

ILLUSTRATION 6.40

A sample of ideal gas ($\gamma = 1.4$) is heated at constant pressure. If 140 J of heat is supplied to gas, find ΔU and W .

Sol. Gas is diatomic as $\gamma = 1.4$, thus, $C_V = \frac{5}{2} R$ and $C_P = \frac{7}{2} R$.

Given, $\Delta H = 140 \text{ J}$ at constant pressure

$$\therefore \Delta H = q_P = n \times C_P \times \Delta T$$

$$\text{Also, } \Delta T = \frac{140}{nC_P} = \frac{140 \times 2}{7n \times R} = \frac{40}{n}$$

$$\text{Now, } W = -nR \Delta T = -n \times 2 \times \frac{40}{n} = -80 \text{ J}$$

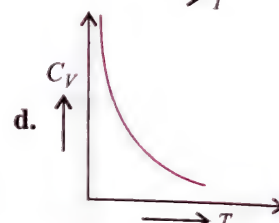
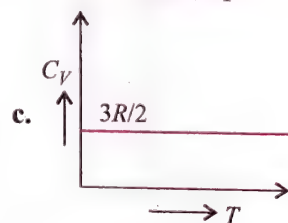
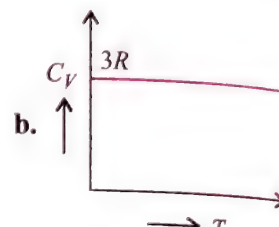
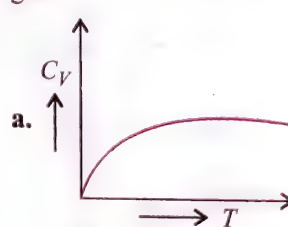
$$\text{Also, } q_P = \Delta H = \Delta U + (-W)$$

$$\Delta U = \Delta H + W = 140 - 80$$

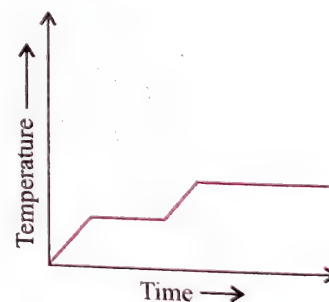
$$\Delta U = 60 \text{ J}$$

ILLUSTRATION 6.41

I. Graph for specific heat at constant volume for a monoatomic gas



II. Heat is supplied to a certain homogeneous sample of matter, at a uniform rate. Its temperature is plotted against time, as shown in the figure below. Which of the following conclusions can be drawn?



a. Its specific heat capacity is greater in the solid state than in the liquid state.

b. Its specific heat capacity is smaller in the solid state than in the liquid state.

c. Its latent heat of vaporisation is greater than its latent heat of fusion.

d. Its latent heat of vaporisation is smaller than its latent heat of fusion.

III. Specific heat at constant pressure of a diatomic gas having molar mass M is approximately equal to

a. $\frac{\gamma R}{M(\gamma - 1)}$

b. $\frac{\gamma}{RM}$

c. $\frac{M}{R(\gamma - 1)}$

d. $\frac{\gamma RM}{\gamma + 1}$

I. c. For monoatomic gas

$$C_V = \frac{3}{2}R$$

II. c. The latent heat of vaporisation is greater than its latent heat of fusion.

III. a. We know that: $C_P - C_V = R$

$$C_P - C_V = \frac{R}{M} \quad \dots(i)$$

$$\frac{C_P}{C_V} = \gamma \quad \dots(ii)$$

Substituting equation (ii) in (i), we get

$$C_P - \frac{C_P}{\gamma} = \frac{R}{M}$$

$$C_P \frac{(\gamma - 1)}{\gamma} = \frac{R}{M}$$

$$C_P = \frac{R\gamma}{(\gamma - 1)M}$$

$$\text{or } \Delta H = \Delta U + \Delta(PV)$$

$$\text{or } \Delta H = \Delta U + \Delta(RT)$$

Since for an isothermal process, ΔU and ΔT are zero hence $\Delta H = 0$

Reversible Isothermal Expansion or Compression

Process

The expression for the work involved in an isothermal expansion or compression from volume V_1 to V_2 can be carried out as follows:

$$\text{Since, } dw = -P dV$$

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, therefore,

$$w = - \int_{V_1}^{V_2} P dV$$

$$\text{For an ideal gas, } P = \frac{nRT}{V}$$

$$\text{So } w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

Integrating,

$$w = -nRT \log_e \frac{V_2}{V_1} = -2.303nRT \log_{10} \frac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$\text{or } \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\text{So } w = 2.303nRT \log_{10} \frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$w_{\text{compression}} = 2.303nRT \log_{10} \frac{V_1}{V_2} = 2.303nRT \log \frac{P_2}{P_1}$$

Hence, for an isothermal expansion or compression, we have

$$q = -w = nRT \ln \frac{P_1}{P_2} = nRT \ln \frac{V_2}{V_1}$$

$$\Delta H = \Delta U = 0$$

Irreversible Isothermal Expansion or Compression Process

Two types of irreversible isothermal expansion or compression processes are observed, i.e., (a) free expansion and (b) intermediate expansion or compression.

a. Free expansion: In free expansion, the external pressure is zero.

$$\therefore P_{\text{ex}} = 0$$

$$\text{Therefore, } w = - \int P_{\text{ex}} dV = 0$$

$$\text{Thus, } q = -w = 0$$

$$\Delta H = \Delta U = 0$$

b. Intermediate expansion or compression: Here, the work is done against constant external pressure.

$$\therefore w = - \int_{V_1}^{V_2} P_{\text{ex}} dV = -P_{\text{ex}}(V_2 - V_1)$$

6.7 CALCULATIONS OF THERMODYNAMIC CHANGES IN EXPANSION OR COMPRESSION OF AN IDEAL GAS

We shall use the first law of thermodynamics to calculate the changes in thermodynamic properties when an ideal gas undergoes the process of expansion or compression. The different types of expansion or compression processes and the corresponding changes in the value of q , w , ΔU , and ΔH are discussed below.

6.7.1 ISOTHERMAL EXPANSION OR COMPRESSION PROCESS

In an isothermal expansion or compression process, the temperature of the system remains constant through out the expansion or compression process, since, for an ideal gas, U depends only on temperature it follows that

$$dU = 0$$

According to the first law of thermodynamics,

$$dU = q + w$$

Since, for an isothermal process, $dU = 0$, we get

$$q = -w$$

This shows that in isothermal expansion or compression heat is converted into work and vice-versa. Work is done by the system at the expense of heat absorbed. (q positive and w negative). If some work is done on the system (w positive), the equivalent amount of heat is given out (q negative).

The magnitude of q or w depends on the manner in which the process of expansion or compression is carried out, i.e., whether it is carried reversibly or irreversibly.

Calculation of ΔH can be done according to the following equation:

$$H = U + PV$$

Hence, in the present case, we have

$$q = -w = P_{\text{ex}}(V_2 - V_1)$$

$$\Delta U = \Delta H = 0$$

Maximum work: The work done by the system always depends upon the external pressure. The higher the value of P_{ex} , the more work is done by the gas. As in expansion, P_{ex} cannot be more than P_{gas} . Under this condition, the work done in reversible expansion is maximum.

On the other hand, the work involved in the intermediate compression process is larger than that involved in the reversible compression. Consequently, more heat will be released in the case of intermediate compression.

6.7.2 ADIABATIC EXPANSION OR COMPRESSION PROCESS

In adiabatic expansion, no heat is allowed to enter or leave the system, hence $q = 0$. When this value is substituted in the first law of thermodynamics, $\Delta U = q + w$, we get $\Delta U = w$.

In expansion, work is done by the system on the surroundings, hence, w is negative. Accordingly, ΔU is also negative, i.e., internal energy decreases and, therefore, the temperature of the system falls. In case of compression, ΔU is positive, i.e., internal energy increases and, therefore, the temperature of the system rises.

Expressions for q , w , ΔU , and ΔH

In adiabatic process, $q = 0$

$$\therefore w = \Delta U$$

The change in the energy can be calculated as follows:

$$\text{Heat capacity } (C_V) = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\text{or } \partial U = C_V \partial T$$

For n mole of ideal gas,

$$\partial U = nC_V \partial T$$

For a finite change, we have

$$\Delta U = U_2 - U_1 = nC_V(T_2 - T_1)$$

The change in enthalpy is given by.

$$\Delta H = \Delta(U + PV)$$

$$= \Delta U + \Delta(PV) = \Delta U + nR \Delta T$$

$$= nC_V(T_2 - T_1) + nR(T_2 - T_1)$$

$$= n(C_V + R)(T_2 - T_1)$$

$$\Delta H = nC_P(T_2 - T_1) \quad [\because C_P = C_V + R]$$

The value of $\Delta T(T_2 - T_1)$ depends upon the process whether it is reversible or irreversible.

6.7.3 GRAPHICAL REPRESENTATION OF FOUR THERMODYNAMIC PROCESSES

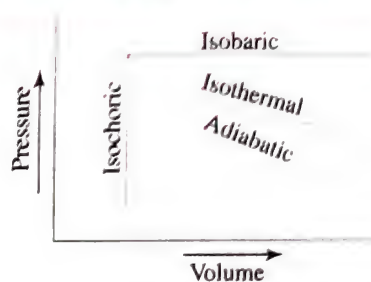


Fig. 6.10

For an Isochoric Process, $\Delta V = 0$

Hence

$$w = -P\Delta V = 0$$

$$\Delta U = q + w$$

$$\Delta U = q$$

$$(\because w = 0)$$

In an isochoric process the heat absorbed will bring a change in internal energy.

For an Adiabatic Process, $q = 0$

\therefore

$$\Delta U = q + w$$

$$\Delta U = 0 + w$$

$$\Delta U = w$$

$$(\because q = 0)$$

In such a case work is done at the cost of internal energy.

- If the gas expands, w is $-ve$, hence internal energy decreases and temperature of the system decreases. Thus, cooling takes place in an adiabatic expansion of the gas.
- If the gas is compressed, w is $+ve$, hence internal energy increases and temperature of the system increases. Thus, heating takes place in an adiabatic contraction of the gas.

For adiabatic change

$$w = \Delta U = C_V \Delta T$$

But

$$w = -P\Delta V$$

$$\therefore -P\Delta V = C_V \Delta T$$

For a reversible adiabatic change

For infinitesimally small quantities, as in reversible expansion,

$$-PdV = C_V dT$$

For 1 mole of a gas $P = RT/V$

$$\frac{-RT}{V} dV = C_V dT$$

$$-R \frac{dV}{V} = C_V \frac{dT}{T}$$

$$\text{Integrating, } -R \int_{V_1}^{V_2} \frac{dV}{V} = C_V \int_{T_1}^{T_2} \frac{dT}{T}$$

$$-R \ln \frac{V_2}{V_1} = C_V \ln \frac{T_2}{T_1} \text{ or } \frac{R}{C_V} \ln \frac{V_1}{V_2} = \ln \frac{T_2}{T_1}$$

Now

$$C_P - C_V = R \text{ and } C_P/C_V = \gamma$$

$$\frac{C_P - C_V}{C_V} \ln \frac{V_1}{V_2} = \ln \frac{T_2}{T_1} \text{ or } (\gamma - 1) \ln \frac{V_1}{V_2} = \ln \frac{T_2}{T_1}$$

$$\ln \left(\frac{V_1}{V_2} \right)^{\gamma-1} = \ln \frac{T_2}{T_1} \text{ or } \left(\frac{V_1}{V_2} \right)^{\gamma-1} = \frac{T_2}{T_1} \quad \dots (i)$$

$$\text{From gas equation } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ or } \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

Substituting in (i),

$$\left(\frac{V_1}{V_2} \right)^{\gamma-1} = \frac{P_2 V_2}{P_1 V_1} \text{ or } \left(\frac{V_1}{V_2} \right)^{\gamma} = \frac{P_2}{P_1}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\text{From gas equation } \frac{V_1}{V_2} = \frac{P_2 T_1}{P_1 T_2}$$

Substituting in (i),

$$\left(\frac{P_2 T_1}{P_1 T_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \quad \text{or} \quad \left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{1-\gamma}$$

Thus, knowing γ , V_1 , V_2 (or P_1 , P_2) and the initial temperature T_1 , the final temperature T_2 can be calculated.

For a monoatomic gas $\gamma = 1.66$ (or $5/3$) for a diatomic gas $\gamma = 1.40$ and for a polyatomic gas $\gamma = 1.33$ (or $4/3$).

For irreversible adiabatic expansion

a. Free expansion. In such a case $P_{\text{ext}} = 0$

$$w = -P\Delta V = -0 \times \Delta V = 0$$

$$\Delta U = w = 0$$

For an ideal change ΔU is a function of temperature

$$\text{i.e., if } \Delta U = 0 \Rightarrow \Delta T = 0$$

$$\Delta H = \Delta U + P\Delta V + V\Delta P \\ = 0 + 0 = 0$$

Thus, for free adiabatic expansion of an ideal gas

$$\Delta H = 0, \Delta U = 0, w = 0 \text{ and } \Delta T = 0$$

b. For intermediate expansion against constant external pressure, P_{ext}

$$-P_{\text{ext}}(V_2 - V_1) = C_V(T_1 - T_2)$$

$$C_V(T_2 - T_1) = P_{\text{ext}}(V_1 - V_2) = P_{\text{ext}} \left(\frac{RT_1}{P_1} - \frac{RT_2}{P_2} \right)$$

$$C_V(T_2 - T_1) = R P_{\text{ext}} \left(\frac{T_1 P_2 - T_2 P_1}{P_1 P_2} \right)$$

6.7.4 COMPARISON BETWEEN ISOTHERMAL REVERSIBLE AND ADIABATIC REVERSIBLE EXPANSION OF AN IDEAL GAS

Consider that a gas from initial stage P_1 and V_1 undergoes isothermal reversible and adiabatic reversible expansion such that the final volumes are the same. Let the final volume be represented by V_f . Let P_{iso} and P_{adi} be the final pressures in the isothermal and adiabatic expansions, respectively. For an isothermal expansion, initial P_1 and V_1 are related to final P_{iso} and V_f as follows:

$$P_1 V_1 = P_{\text{iso}} V_f$$

$$\text{or } \frac{V_f}{V_1} = \frac{P_1}{P_{\text{iso}}} \quad \dots(i)$$

In adiabatic expansion, these variables are related as:

$$P_1 V_1^{\gamma} = P_{\text{adi}} V_f^{\gamma}$$

$$\text{or } \left(\frac{V_f}{V_1}\right)^{\gamma} = \left(\frac{P_1}{P_{\text{adi}}}\right) \quad \dots(ii)$$

Since for an expansion $V_f > V_1$ and the fact that $\gamma > 1$, we have on comparing equations (i) and (ii)

$$\left(\frac{V_f}{V_1}\right)^{\gamma} > \left(\frac{V_f}{V_1}\right)$$

so that

$$\frac{P_1}{P_{\text{adi}}} > \frac{P_1}{P_{\text{iso}}} \\ \text{or } P_{\text{adi}} < P_{\text{iso}} \quad \dots(iii)$$

Since the work done in expansion depends upon the pressure, hence work done in reversible isothermal expansion is greater than that in reversible adiabatic expansion.

The two expansions are shown in Fig. (6.11). The magnitude of the work involved is equal to the area under the curve. It can be seen from this figure that the magnitude of the work involved in the isothermal expansion is greater than that involved in the adiabatic expansions.

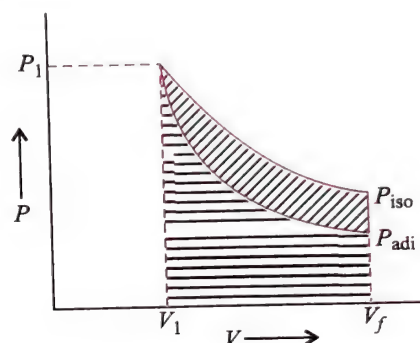


Fig. 6.11 Comparison of magnitude of work involved in isothermal and adiabatic expansions

This also follows from the fact that in the adiabatic expansion, temperature falls whereas in isothermal expansion, temperature remains the same. Since the final volumes are the same, according to Charles' law ($P \propto T$, V constant), P_{adi} will be smaller than P_{iso} and thus the magnitude of the reversible work involved from volume V_1 to V_f ($V_f > V_1$) for an ideal gas is greater in the isothermal process than that involved in the adiabatic process.

Let us consider now the expansion in which the final pressure P_f is the same. Let V_{iso} and V_{adi} be the final volumes in isothermal and adiabatic expansions, respectively.

For an isothermal expansion

$$P_1 V_1 = P_f V_{\text{iso}}$$

$$\text{or } \left(\frac{P_1}{P_f}\right) = \frac{V_{\text{iso}}}{V_1} \quad \dots(i)$$

For an adiabatic expansion

$$P_1 V_1^{\gamma} = P_f V_{\text{adi}}^{\gamma}$$

$$\text{or } \left(\frac{P_1}{P_f}\right) = \left(\frac{V_{\text{adi}}}{V_1}\right)^{\gamma} \quad \dots(ii)$$

Comparing equation (i) and (ii), we get

$$\frac{V_{\text{iso}}}{V_1} = \left(\frac{V_{\text{adi}}}{V_1}\right)^{\gamma}$$

$$\text{or } \ln \frac{V_{\text{iso}}}{V_1} = \gamma \ln \left(\frac{V_{\text{adi}}}{V_1}\right)$$

Since $\gamma > 1$, it follows that

$$\frac{V_{\text{iso}}}{V_1} > \frac{V_{\text{adi}}}{V_1} \quad \text{or } V_{\text{adi}} < V_{\text{iso}}$$

Hence, in an adiabatic expansion, final volume is less than that of an isothermal expansion.

This also follows from the fact that in adiabatic expansion,

temperature falls whereas in isothermal expansion, it remains the same and since the final pressure are the same, therefore according to Charles, law ($V \propto T$, P constant), V_{adi} will be smaller than V_{iso} .

Table 6.2 Comparison of thermodynamic quantities in different types of adiabatic process

Expansion	w	T	ΔU	ΔH
Reversible	$w = nC_V(T_2 - T_1) < 0$	$T_2 < T_1$	$\Delta U = nC_V(T_2 - T_1) < 0$	$\Delta H = nC_P(T_2 - T_1) < 0$
Intermediate	$w' = nC_V(T_2 - T_1) < 0$	$T_2 < T_1$	$\Delta U' = nC_V(T_2 - T_1) < 0$	$\Delta H' = nC_P(T_2 - T_1) < 0$
Free	$w'' = nC_V(T_2 - T_1) = 0$	$T_2' = T_1$	$\Delta U'' = nC_V(T_2 - T_1) = 0$	$\Delta H'' = 0$

a. $T_2 < T_2' < T_2'' = T_1$

d. $\Delta U < \Delta U' < \Delta U''$

b. $w < w' < w''$

e. $\Delta H < \Delta H' < \Delta H''$

c. $|w| > |w'| > |w''|$

f. $|\Delta H| > |\Delta H'| > |\Delta H''|$

$PV^\gamma = \text{constant}$

and $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$, where $\gamma = \frac{C_P}{C_V}$

Work involved in an isothermal expansion is greater than that involved in an adiabatic expansion.

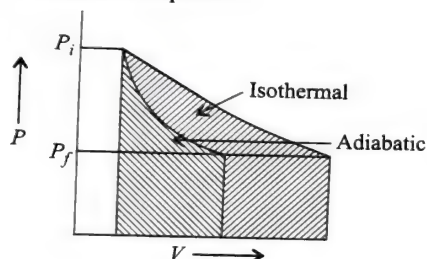


Fig. 6.12 Comparison of the magnitude of the work involved in isothermal and adiabatic expansions

Fig. (6.12) shows the two expansions. The magnitude of the work involved in an isothermal expansion is greater than that involved in an adiabatic expansion.

6.7.5 JOULE'S THOMSON EFFECT

When a **real gas** at a certain pressure expands adiabatically through a porous plug or fine hole into region of low pressure, it is accompanied by cooling (except for hydrogen and helium which get warmed up). For an **ideal gas** there is no heating or cooling during an adiabatic expansion or contraction.

During expansion, the enthalpy of system remains constant. Mathematically, the Joule Thomson coefficient is given as

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H$$

It is defined as the temperature change in degrees produced by a drop of one atmospheric pressure when the gas expands under conditions of constant enthalpy.

(i) For cooling, $\mu > 0$ (-ve sign) (ii) For heating, $\mu < 0$ (+ve sign)

For $\mu = 0$, the gas neither gets heated nor cooled.

Every gas has a definite value of temperature at which the sign of μ changes from -ve to +ve. Such a temperature is termed

as **inversion temperature**. It is the temperature below which a gas becomes cooler on expansion.

For most of the gases, inversion temperature is near the room temperature. Thus these get cooled at room temperature when expansion occur.

For hydrogen (-80°C) and helium (-240°C), the inversion temperature is negative. Thus these get warmed up on expansion.

6.7.6 CLAUSIUS-CLAPEYRON EQUATION

For liquid m Vapour equilibrium

$$\log \frac{P_2}{P_1} = \frac{\Delta H_V}{2.303R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

where ΔH_V is enthalpy of vaporisation and P_1 and P_2 are the vapour pressures at temperatures T_1 and T_2 respectively at the boiling points at pressure P_1 and P_2 respectively.

6.7.7 EXPLOSION TEMPERATURE

If the combustion is carried under adiabatic conditions at constant volume, the maximum temperature attained is called explosion temperature.

MISCELLANEOUS QUESTIONS

ILLUSTRATION 6.42

14 g oxygen at 0°C and 10 atm is subjected to reversible adiabatic expansion to a pressure of 1 atm. Calculate the work done in

a. Litre atmosphere.

b. Calorie (given, $C_P/C_V = 1.4$).

Sol. $P_1 = 10$ atm at $T = 273$ K for $\frac{14}{32}$ mol O_2 .

$P_2 = 1$ atm at $T = T_2$ for $\frac{14}{32}$ mol O_2 .

For adiabatic expansion, we have $T^\gamma \cdot P^{1-\gamma} = \text{Constant}$

$$\therefore \left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^{1-\gamma} \text{ or } \gamma \log \frac{T_1}{T_2} = (1-\gamma) \log \frac{P_2}{P_1}$$

$$\text{or } 1.4 \log \frac{273}{T_2} = (1 - 1.4) \log \frac{1}{10} \Rightarrow T_2 = 141.4 \text{ K}$$

$$\text{Work done in adiabatic expansion} = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$$

$$\ln \text{L-atm} = \frac{14}{32} \times \frac{0.0821(141.4 - 273)}{(1.4 - 1)}$$

$$W_{\text{rev}} = -11.82 \text{ L-atm}$$

$$\ln \text{cal} = \frac{14}{32} \times \frac{2 \times (141.4 - 273)}{(1.4 - 1)}$$

$$W_{\text{rev}} = -287.88 \text{ cal}$$

ILLUSTRATION 6.43

When a polyatomic gas undergoes an adiabatic process, its temperature and volume are related by the equation $TV^n = \text{constant}$, the value of n will be

- a. 1.33 b. 0.33 c. 2.33 d. 1

b. For adiabatic process

$$TV^{\gamma-1} = \text{constant}$$

for poly atomic gas

$$\gamma = \frac{4}{3} = 1.33 \quad \left(\gamma = \frac{C_P}{C_V} \right)$$

$$n = 1.33 - 1 = 0.33$$

ILLUSTRATION 6.44

A mono atomic gas X and a diatomic gas Y both initially at the same temperature and pressure are compressed adiabatically from a volume V to $V/2$. Which gas will be at higher temperature?

- a. X b. Y
c. both are same d. Cannot be determined

$$a. T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 2^{\gamma-1}$$

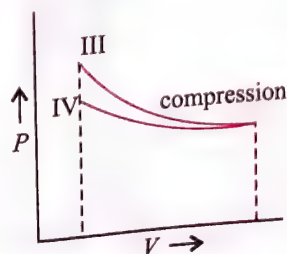
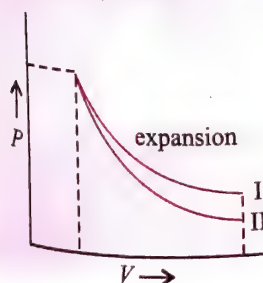
Since γ is more for the gas X , the temperature will also be more for it.

ILLUSTRATION 6.45

I. In a thermodynamic process helium gas obeys the law $T/P^{2/5} = \text{constant}$. The heat given n moles of He in order to raise the temperature from T to $2T$ is

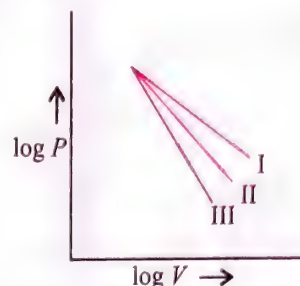
- a. $8RT$ b. $4RT$ c. $16RT$ d. Zero

II. Which of the following graphs given below show(s) adiabatic process?



- a. II, III b. I, III c. II, IV d. I, IV

III. The following curves represent adiabatic expansions of gases He, O_2 , and O_3 not necessarily in order. Which curve represents for O_3 ?



- a. I b. II
c. III d. Any one of these
- IV. During an adiabatic expansion, a gas obeys $VT^3 = \text{constant}$. The gas must be
- a. Monoatomic b. Diatomic
c. Polyatomic d. Either of these

Sol.

$$I. d. T = K \times P^{2/5}$$

$$\therefore PV = RT = R \cdot K \cdot P^{2/5} \text{ or } P^{3/5} \times V = K \text{ or } PV^{5/3} = K' \text{ or } PV^\gamma = K' \quad (\gamma \text{ for He} = 5/3)$$

$$\therefore \text{Process is adiabatic and } \Delta H = 0.$$

II. a. Adiabatic slopes are more steeper than isothermal. Slope of adiabatic process = $\gamma \times$ Slope of isothermal process.

III. a. $PV^\gamma = \text{constant}$ or $\log P = -\gamma \log V$
 γ is slope for P - V plots for He, O_2 , and O_3 , i.e., $\frac{5}{3}, \frac{7}{5}$ and $\frac{4}{3}$, respectively.

IV. c. $VT^3 = \text{constant}$,
Also $V^{\gamma-1}T = \text{constant}$ for adiabatic expansion.

$$V \cdot T^{\frac{1}{\gamma-1}} = \text{constant} \text{ or } \frac{1}{\gamma-1} = 3$$

$$\gamma = \frac{4}{3}, \text{ i.e., polyatomic gas.}$$

ILLUSTRATION 6.46

Show that in an isothermal expansion of an ideal gas,
a. $\Delta U = 0$ and b. $\Delta H = 0$.

Sol.

a. For one mole of an ideal gas, $C_V = \left(\frac{\partial U}{\partial T} \right)_V$

Hence,

$$\Delta U = C_V dT$$

$$\text{For a finite change, } \Delta U = C_V \Delta T$$

For an isothermal process, T is constant so that $\Delta T = 0$
Therefore, $\Delta U = 0$.

b. We know that, $\Delta H = \Delta U + \Delta(PV)$

For an ideal gas, $PV = RT$

$$\therefore \Delta H = \Delta U + \Delta(RT) = \Delta U + R \Delta T$$

Since $\Delta T = 0$ and $\Delta U = 0$

Therefore, $\Delta H = 0$

ILLUSTRATION 6.47

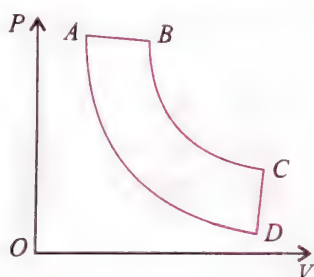
I. For adiabatic expansion of a perfect gas, $\frac{dP}{P}$ is

- a. $\frac{dV}{V}$ b. $\gamma \cdot \frac{dV}{V}$ c. $-\gamma \frac{dV}{V}$ d. $-\gamma^2 \frac{dV}{V}$

II. He, N_2 , and O_3 are expanded adiabatically and their expansion curves between P and V are plotted under similar conditions. About the ratio of the slopes, which one is not correct?

- a. The ratio of slopes of P-V curves for He and O_3 is 1.25.
b. The ratio of slopes of P-V curves for He and N_2 is 1.20.
c. The ratio of slopes of P-V curves for N_2 and O_3 is 1.05.
d. The slope of He is least steeper and for O_3 is most steeper.

III. In the pressure-volume diagram given below, the isochoric, isothermal, isobaric, and isentropic parts, respectively, are:



- a. BA, AD, DC, CB b. DC, CB, BA, AD
c. AB, BC, CD, DA d. CD, DA, AB, BC

Sol.

I. c. For adiabatic expansion, $PV^\gamma = \text{constant}$

$$\text{On differentiating, } P \cdot \gamma \cdot V^{\gamma-1} dV + V^\gamma dP = 0$$

$$-P \gamma V^{\gamma-1} dV = V^\gamma dP$$

$$\text{or } \frac{dP}{P} = -\gamma \cdot \frac{V^{\gamma-1}}{V^\gamma} dV = -\gamma \cdot \frac{dV}{V}$$

II. d. Ratio of slope = $\frac{\gamma \text{ for gas I}}{\gamma \text{ for gas II}}$; slope for He, N_2 and O_3 are 7/5, 5/4, and 4/3, respectively.

III. d. CD—Isochoric (at constant volume)
DA—Isothermal compression ($\Delta T = 0$)
AB—Isobaric (at constant pressure)
BC—Isoentropic (at constant entropy)

ILLUSTRATION 6.48

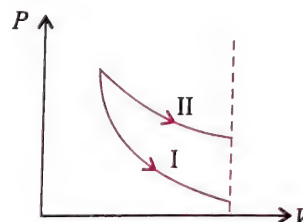
A gas is expanded from volume V_1 to V_2 through three different processes:

- I. Reversible adiabatic
II. Reversible isothermal
III. Irreversible adiabatic (against a constant external pressure P_{ex})

The correct option is

- a. $[(T_f)_{\text{Gas}}]_{\text{Reversible isothermal}} > [(T_f)_{\text{Gas}}]_{\text{Reversible adiabatic}} > [(T_f)_{\text{Gas}}]_{\text{Irreversible adiabatic}}$
b. $[(T_f)_{\text{Gas}}]_{\text{Reversible isothermal}} > [(T_f)_{\text{Gas}}]_{\text{Irreversible adiabatic}} > [(T_f)_{\text{Gas}}]_{\text{Reversible adiabatic}}$
c. $w_{\text{Reversible isothermal}} > w_{\text{Irreversible adiabatic}} > w_{\text{Reversible adiabatic}}$
d. $(P_f)_{\text{Reversible isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$

Sol. b. $w_{\text{Isothermal}} > w_{\text{Adiabatic}}$ and $w_{\text{Rev.}} > w_{\text{Irr.}}$
(Rev.) (II) (Rev.) (I)



$$\Rightarrow W_{\text{Rev. isothermal}} > W_{\text{Rev. adiabatic}} > W_{\text{irr. adiabatic}}$$

In isothermal expansion, $T = \text{constant}$

In adiabatic expansion, $T \downarrow$. More is the work done by the gas, more is the decrease in T .

(\because Work is being done at the expense of ΔU)

CONCEPT APPLICATION EXERCISE 6.2

Subjective Type

1. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant external pressure of 3.0 atm . The work done during the expansion is used to heat 10.0 mL of water of temperature 290.0 K . Calculate the final temperature of water (specific heat of water = $4.184 \text{ J g}^{-1} \text{ K}^{-1}$).
2. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 L to a volume of 6 L . In doing so, it absorbs 800 J heat from the surroundings. Determine the increase in internal energy of process.
3. Calculate q , w , ΔU , and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 127°C from a volume of 20 dm^3 to 40 dm^3 .
4. An insulated container contains 1 mole of a liquid, molar volume 100 mL at 1 bar . When liquid is steeply passed to 100 bar , volume decreases to 99 mL . Find ΔH and ΔU for the process.

Objective Type

5. 5 mol of an ideal gas at 27°C expands isothermally and reversibly from a volume of 6 L to 60 L . The work done in kJ is
(1) -14.7 (2) -28.72 (3) $+28.72$ (4) -56.72

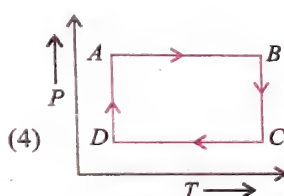
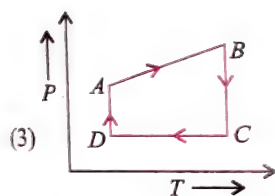
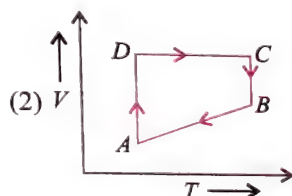
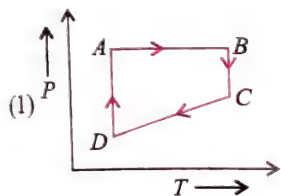
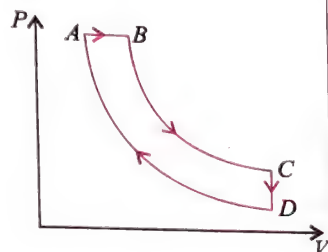
6. 10 mol of an ideal gas confined to a volume of 10 L is released into atmosphere at 300 K where the pressure is 1 bar. The work done by the gas is ($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

(1) 249 L bar (2) 259 L bar (3) 239 L bar (4) 220 L bar

7. A system absorbs 20 kJ heat and also does 10 kJ of work. The net internal energy of the system

(1) Increases by 10 kJ (2) Decreases by 10 kJ
(3) Increases by 30 kJ (4) Decreases by 30 kJ

8. A cyclic process ABCD is shown in the P - V diagram. Which of the following curves represents the same process?

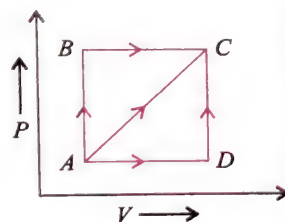


9. A thermodynamic process is shown in the following figure. The pressure and volumes corresponding to some points in the figure are:

$$P_A = 3 \times 10^4 \text{ Pa},$$

$$V_A = 2 \times 10^{-3} \text{ m}^3;$$

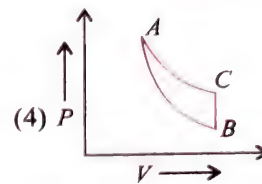
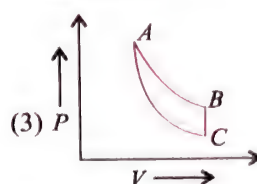
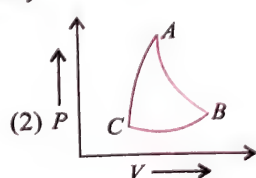
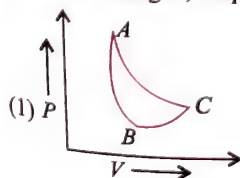
$$P_E = 8 \times 10^4 \text{ Pa}, V_D = 5 \times 10^{-3} \text{ m}^3$$



In process AB, 600 J of heat is added to the system and in the process BC, 200 J of heat is added to the system. The change in internal energy of the system in the process AC would be

(1) 560 J (2) 800 J (3) 600 J (4) 640 J

10. In which of the following indicator diagrams given below do AB, BC, and CA represent isothermal, isochoric, and adiabatic changes, respectively?



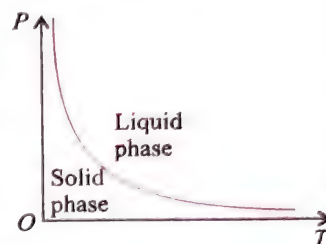
11. The pressure-temperature (P - T) phase diagram shown below corresponds to the

(1) Curve of fusion of solids that expand on solidification.

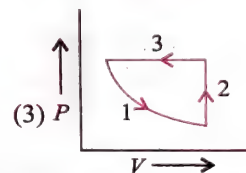
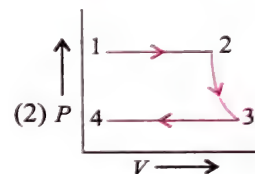
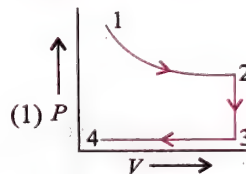
(2) Curve of sublimation of solids that directly go over to the vapour phase.

(3) Both (1) and (2)

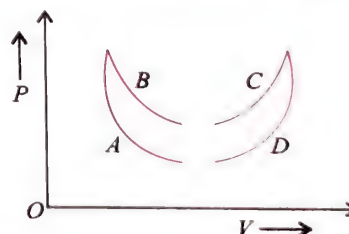
(4) None of these



12. An ideal gas undergoes isothermal expansion followed by heat removal at constant volume and then by heat removal at constant pressure to the initial volume. The correct description of these steps is indicated by



13. Four curves A, B, C, and D are drawn in figure for a given amount of gas. The curve which represents adiabatic and isothermal changes, respectively, is



(1) C and D

(2) D and C

(3) A and B

(4) B and A

ANSWERS

Subjective Type

1. 290.81 K

2. 394.95 J

3. $\Delta U = \Delta H = 0$

$q = 2305.3 \text{ J}$

$w = -2305.3 \text{ J}$

4. $\Delta U = 100 \text{ bar mL}^{-1}$; $\Delta H = 9900 \text{ bar mL}^{-1}$

Objective Type

5. (2)

6. (3)

7. (1)

8. (1)

9. (2)

10. (3)

11. (1)

12. (1)

13. (3)

6.8 THERMOCHEMISTRY

Thermochemistry is a branch of physical chemistry which is concerned with energy change between a chemical system and its surroundings when a change of phase or a chemical reaction takes place within the system. It is also termed as *chemical energetics*. It is based on the first law of thermodynamics.

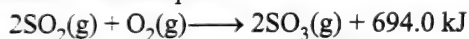
Chemical reactions are accompanied by evolution or absorption of heat energy. When reactants combine together to form new products, there is readjustment of energies. During a chemical reaction, the chemical bonds between atoms in the reactant molecules are rearranged in the product molecules, i.e., chemical bonds in the reactants are broken down and new chemical bonds are formed in the products. Energy is needed to break the bonds of reactants and energy is released in the formation of new bonds of products.

6.8.1 THERMOCHEMICAL EQUATIONS

A chemical equation is a brief representation of a chemical change in terms of symbols or formulae of reactants and products. When the heat change accompanying the chemical reaction is also included in the chemical equation, it is known as thermochemical equation. Thus, a thermochemical equation may be defined as a chemical equation which indicates the amount of heat evolved or absorbed during the chemical reaction in addition to the quantities of reactants or products.

A thermochemical equation can be written in two ways:

- Heat effect can be written as one of the term along with the products. For example:



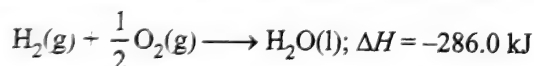
- Heat evolved or absorbed can be expressed in terms of ΔH .

For example:

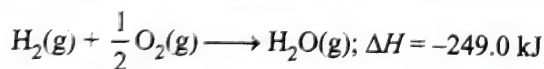


Physical states of various reactants and products must be mentioned while writing thermochemical equations because change of state is also accompanied by the enthalpy changes, and the reactants and products must have the same temperature and pressure. For example:

When 1 mol of H_2 gas reacts with $1/2$ mol of O_2 gas to produce 1 mol of liquid water, 286.0 kJ of heat is produced.

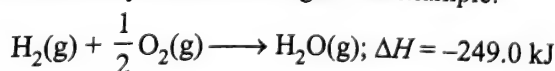


On the other hand, if 1 mol of water vapour is produced instead of 1 mol of liquid water, the value of ΔH will be different.

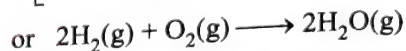
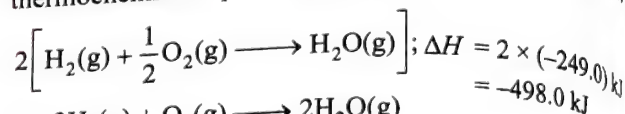


Important Features about Thermochemical Equations

- The coefficients of various substance of chemical equation represents the number of their respective moles.
- The value of ΔH in a thermochemical equation corresponds to the enthalpy change with a specified number of moles of various reactants and products are involved in the reaction.
- If the coefficients in the chemical equations are multiplied or divided by some integer, the ΔH value also be multiplied or divided by the same integer. For example:

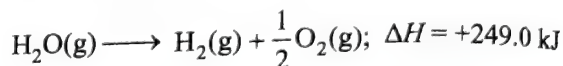
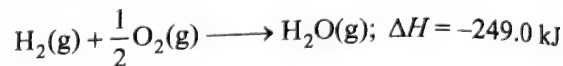


If the whole equation is multiplied by 2, the ΔH for the new thermochemical equation is given as



- When a chemical equation is reversed, the magnitude of the ΔH remains same, however, its sign is reversed.

For example, if ΔH is +ve for the forward reaction, it would be negative for the reverse reaction.

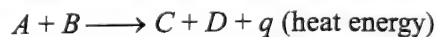


6.8.2 EXOTHERMIC AND ENDOTHERMIC REACTIONS

There are many reactions in which energy is evolved while in others energy is absorbed. Depending upon the evolution or absorption of energy, the chemical reaction can be classified into two types: exothermic and endothermic reactions.

- Exothermic reactions:** The chemical reactions which proceed with the evolution of heat energy are called exothermic reactions.

In general, exothermic reactions may be represented as:



The heat evolved is expressed in units of Joules (J) or kilo Joules (kJ).

At constant temperature and constant volume, heat evolved is equal to internal energy change (ΔU). For exothermic reactions, there is evolution of heat energy and consequently the energy of the products (ΣU_P) becomes less than internal energy of the reactants (ΣU_R). Thus, ΔU will be negative

$$\Delta U = \Sigma U_P - \Sigma U_R$$

$$\text{As } \Sigma U_P < \Sigma U_R$$

$$\therefore \Delta U = -\text{ve}$$

For example:



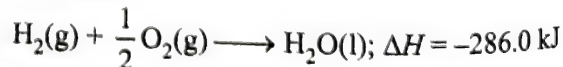
At constant temperature and pressure, the heat evolved is equal to enthalpy change (ΔH).

$$\Delta H = \Sigma H_P - \Sigma H_R$$

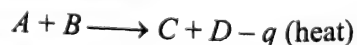
In exothermic reaction, $\Sigma H_P < \Sigma H_R$

$$\therefore \Delta H = -\text{ve}$$

For example:



- Endothermic reaction:** The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. In general, an endothermic reaction can be represented as:

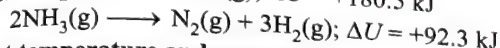
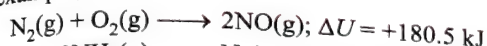


As constant temperature and constant volume

$$\Delta U = \Sigma U_P - \Sigma U_R = +\text{ve}$$

as $\Sigma U_P > \Sigma U_R$

For example;

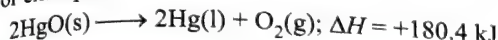


A constant temperature and constant pressure

$$\Delta H = \Sigma H_P - \Sigma H_R, \text{ as } \Sigma H_P > \Sigma H_R$$

$$\therefore \Delta H = +ve$$

For example:



Sign convention:

For exothermic reaction: ΔU or $\Delta H = -ve$

For endothermic reaction: ΔU or $\Delta H = +ve$

6.9 HEAT OF REACTION OR ENTHALPY OF REACTION

Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (or heat of reaction)

$$= \Delta H = \Sigma H_P - \Sigma H_R$$

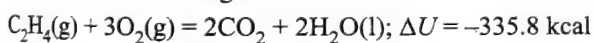
For example, the equation



$$\text{or } \Delta H = -44 \text{ kcal}$$

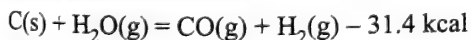
indicates that when 2 g of hydrogen (1 mol) completely reacts with 71 g of chlorine (1 mol) to form 73 g of HCl (2 mol), the amount of heat evolved is 44.0 kcal or the enthalpy decreases by 44.0 kcal or the reacting system loses 44.0 kcal of heat or the enthalpy change of the reaction, $\Delta H = -44.0 \text{ kcal}$.

Consider the following reaction:



The equation indicates that reaction has been carried between 1 mol of C_2H_4 and 3 mol of oxygen at constant volume and 25°C . The heat evolved is 335.8 kcal or the internal energy of the system decreases by 335.8 kcal.

Consider another reaction:



$$\text{or } \Delta H = 31.4 \text{ kcal}$$

This reaction indicates that 1 mol of carbon (12 g) reacts with 1 mol of steam (18 g) to form 1 mol of CO and 1 mol of hydrogen and 31.4 kcal of heat is absorbed. The enthalpy of the system increases by 31.4 kcal or the total enthalpy of the products is 31.4 kcal more than the enthalpy of reactants.

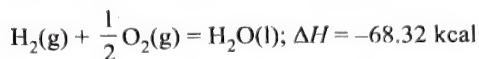
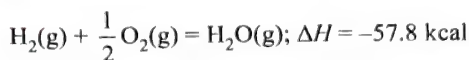
6.9.1 FACTORS THAT INFLUENCE THE ENTHALPY OF REACTION

There are a number of factors that affect the magnitude of the enthalpy of reaction:

a. Physical state of reactants and products: Heat energy is involved for changing the physical state of a chemical

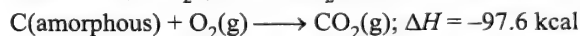
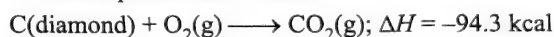
substance. For example in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed.

Considering the following two reactions:

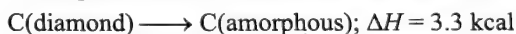


It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in the second case is higher because heat is evolved when steam condenses. Hence, physical state always affects the heat of reaction.

b. Allotropic forms of the element: Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.



The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is termed as *heat of transition*.



c. Temperature: Heat of reaction or enthalpy of reaction also depends on the temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature. Due to this reason, enthalpies of reaction are calculated and expressed at a standard temperature of 25°C or 298 K. However, if the reaction is not carried out at 25°C , the temperature at which the reaction is performed is indicated.

d. Reaction carried out at constant pressure or constant volume: When a chemical reaction occurs at constant volume, the heat change is called the enthalpy of reaction at constant volume. However, most of the reactions are carried out at constant pressure. The enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions that involve gases, the difference in two values is considerable.

$$\Delta U + \Delta nRT = \Delta H$$

$$\text{or } q_V + \Delta nRT = q_P$$

q_V = Heat change at constant volume

q_P = Heat change at constant pressure

Δn = Total number of moles of products – Total number of moles of reactants

e. Quantities of reactant: The amount of heat evolved or absorbed depends upon the amount of reactants. For example, combustion of 12 g (1 mol) of carbon produces 393.5 kJ of heat, while combustion of 1.2 g of carbon produces 39.35 kJ of heat.

6.9.2 KIRCHOFF'S RELATION (VARIATION OF ENTHALPY OF A REACTION WITH TEMPERATURE)

The variation of enthalpy of reaction with temperature is given by Kirchhoff's equation.

Consider a process



U_A and H_A are the internal energy and enthalpy of A , respectively, whereas U_B and H_B are the internal energy and enthalpy of B , respectively

Hence,

$$\Delta H = H_B - H_A$$

Since enthalpy is a function of temperature and pressure, we can differentiate the above equation with respect to temperature at constant pressure, i.e.,

$$\left[\frac{\delta(\Delta H)}{dT} \right]_P = \left[\frac{\delta(H_B)}{dT} \right]_P - \left[\frac{\delta(H_A)}{dT} \right]_P \\ = (C_P)_B - (C_P)_A = \Delta C_P$$

where ΔC_P = difference in the heat capacity between reactants and products

$$\text{or } d(\Delta H) = \Delta C_P \cdot dT \quad \dots(i)$$

Case I: When ΔC_P is constant between two temperatures T_1 and T_2 .

$$\therefore \int_{H_1}^{H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P \cdot dT$$

$$\text{or } [\Delta H]_{H_1}^{H_2} = \Delta C_P (T_2 - T_1)$$

$$\text{or } \Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1) \quad \dots(ii)$$

Similarly, we can write,

$$\Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1) \quad \dots(iii)$$

Equations (ii) and (iii) are known as Kirchhoff's equations.

Case II: ΔC_P varies with temperature

$$\int d(\Delta H) = \Delta C_P \cdot dT$$

$$\text{or } \Delta H = \int \Delta C_P dT + K$$

where K is the integration constant.

when $T = 0$, then $\Delta H_0 = K$

$$\therefore \Delta H = \Delta H_0 + \int \Delta C_P dT \quad \dots(iv)$$

where ΔH_0 refers to the enthalpy change at absolute zero.

$$\text{or } \Delta H = \Delta H_0 + \alpha T + \beta \frac{T^2}{2} + \gamma \frac{T^3}{3} \quad \dots(v)$$

Equations (i) and (v) are another form of Kirchhoff's equations.

6.9.3 STANDARD ENTHALPY OF REACTION ($\Delta_r H^\ominus$)

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

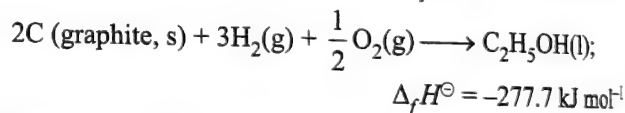
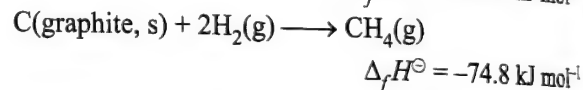
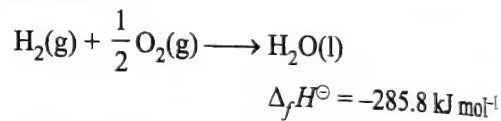
The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript \ominus to the symbol ΔH , e.g., $\Delta_r H^\ominus$.

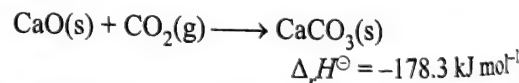
6.10 TYPES OF ENTHALPIES OF REACTION

6.10.1 STANDARD ENTHALPY OF FORMATION ($\Delta_f H^\ominus$)

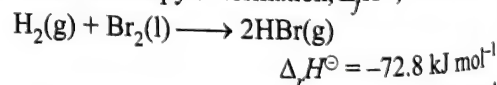
The standard enthalpy change for the formation of one mole of a compound from its element in their most stable states of aggregation (also known as reference states) is called standard molar enthalpy of formation. Its symbol is $\Delta_f H^\ominus$, where the subscript 'f' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon, and sulphur is O_2 gas, C_{graphite} and S_{rhombic} respectively. Some reactions with standard molar enthalpies of formation are given below.



It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^\ominus$, is just a special case of $\Delta_r H^\ominus$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane, and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:

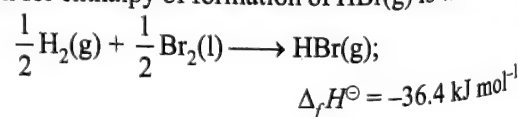


is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not the standard enthalpy of formation, $\Delta_f H^\ominus$, for $HBr(g)$.



Here two moles, instead of one mole of the product is formed from the elements, i.e., $\Delta_r H^\ominus = 2\Delta_f H^\ominus$.

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of $HBr(g)$ is written as

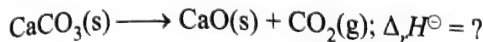


Standard enthalpies of formation of some common substances are given in Appendix (Table A6).

Importance of standard enthalpies of formation

The knowledge of standard enthalpies of various substances can be used to calculate standard enthalpy change of any reaction. For example:

To calculate the heat required to decompose calcium carbonate to lime and carbon dioxide, with all the substance in their standard state.



The following general equation can be used for the enthalpy change calculation:

$$\Delta_r H^\ominus = \sum_i a_i \Delta_f H^\ominus (\text{products}) - \sum_i b_i \Delta_f H^\ominus (\text{reactants})$$

where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients a and b are 1 each.

Therefore,

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus [\text{CaO}(\text{s})] + \Delta_f H^\ominus [\text{CO}_2(\text{g})] \\ &\quad - \Delta_f H^\ominus [\text{CaCO}_3(\text{s})] \\ &= 1(-635.1 \text{ kJ mol}^{-1}) + 1(-393.5 \text{ kJ mol}^{-1}) \\ &\quad - 1(-1206.9 \text{ kJ mol}^{-1}) \\ &= 178.3 \text{ kJ mol}^{-1} \end{aligned}$$

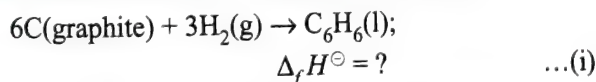
Thus, the decomposition of $\text{CaCO}_3(\text{s})$ is an endothermic process and CaCO_3 should be heated for getting the products.

QUESTION BASED ON STANDARD ENTHALPY OF FORMATION ($\Delta_f H^\ominus$) AND COMBUSTIONS ($\Delta_c H^\ominus$)

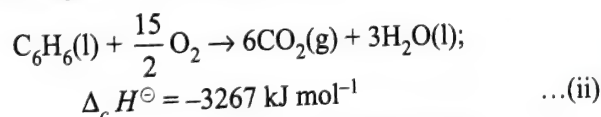
ILLUSTRATION 6.49

The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\ominus$ of benzene. Standard enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are $-393.5 \text{ kJ mol}^{-1}$ and $-285.83 \text{ kJ mol}^{-1}$ respectively.

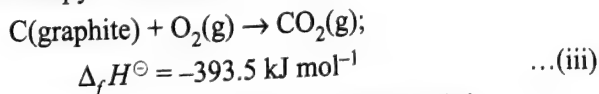
Sol. The formation reaction of benzene is given by:



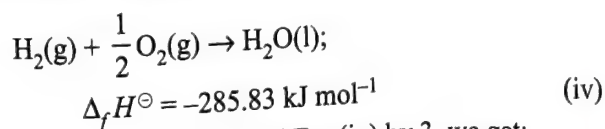
The enthalpy of combustion of 1 mol of benzene is:



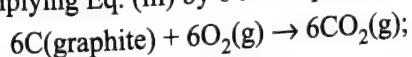
The enthalpy of formation of 1 mol of $\text{CO}_2(\text{g})$:



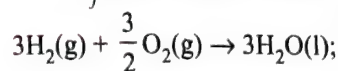
The enthalpy of formation of 1 mol of $\text{H}_2\text{O}(\text{l})$ is:



Multiplying Eq. (iii) by 6 and Eq. (iv) by 3, we get:

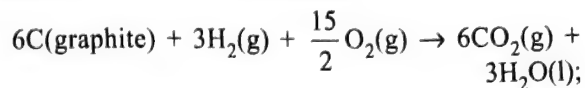


$$\Delta_f H^\ominus = -2361 \text{ kJ mol}^{-1}$$



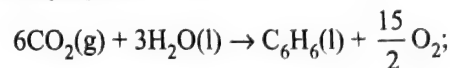
$$\Delta_f H^\ominus = -857.49 \text{ kJ mol}^{-1}$$

Summing up the above two equations:



$$\Delta_r H^\ominus = -3218.49 \text{ kJ mol}^{-1} \quad \dots(\text{v})$$

Reversing equation (ii);



$$\Delta_r H^\ominus = 32.67.0 \text{ kJ mol}^{-1} \quad \dots(\text{vi})$$

Adding equations (v) and (vi), we get

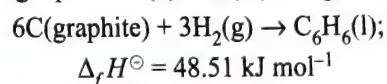
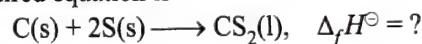


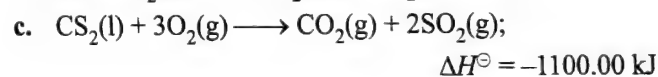
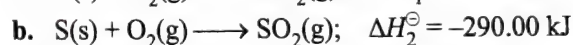
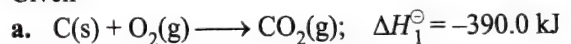
ILLUSTRATION 6.50

Calculate the standard heat of formation of carbon disulphide (CS_2). Given that the standard heats of combustion of carbon (s), sulphur (s) and carbon disulphide (CS_2) are -390.0 , 290.0 , and $-1100.0 \text{ kJ mol}^{-1}$, respectively.

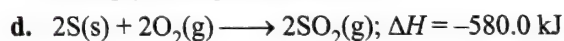
Sol. Required equation is



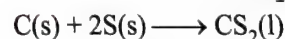
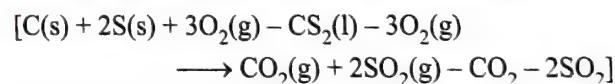
Given



Multiply the equation (b) by 2.



Adding equation (a) and (d) and subtracting (c),



$$\Delta_f H^\ominus = \Delta H_1^\ominus + 2\Delta H_2^\ominus - \Delta H_3^\ominus$$

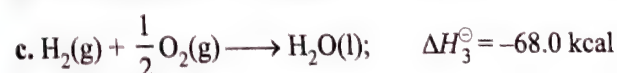
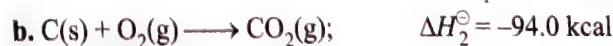
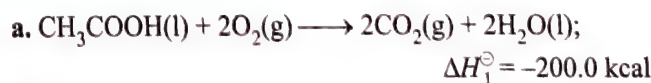
This is the required equation.

$$\text{Thus, } \Delta_f H^\ominus = -390.0 - 580.0 + 1100.0 = 130.00 \text{ kJ}$$

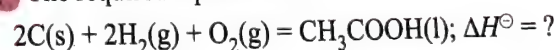
Standard heat of formation of $\text{CS}_2(\text{l}) = 130.00 \text{ kJ}$

ILLUSTRATION 6.51

Calculate the heat of formation of acetic acid from the following data:



Sol. The required equation is



This equation can be obtained by multiplying equation (iii) by 2 and also equation (c) by 2 and adding both and finally subtracting equation (a).

$$\Delta H^\ominus = 2\Delta H_2^\ominus + 2\Delta H_3^\ominus - \Delta H_1^\ominus$$

$$[2C + 2O_2 + 2H_2O + O_2 - CH_3COOH(l) - 2O_2] \longrightarrow 2CO_2 + 2H_2O - 2CO_2 - 2H_2O$$

$$\Delta H^\ominus_{CH_3COOH(l)} = 2 \times (-94.0) + 2 \times (-68.0) - (-200.0)$$

$$= -188.00 - 136.0 + 200.0$$

$$= -324.0 + 200.0$$

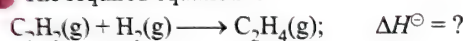
$$= -124.0 \text{ kcal}$$

ILLUSTRATION 6.52

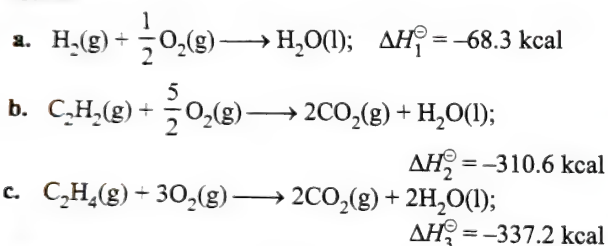
Given the following standard heats of reactions:

(a) heat of formation of water = -68.3 kcal , (b) heat of combustion of $C_2H_2 = -310.6 \text{ kcal}$, (c) heat of combustion of ethylene = -337.2 kcal . Calculate the heat of reaction for the hydrogenation of acetylene at constant volume and at 25°C .

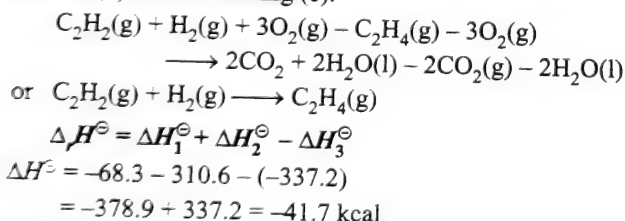
Sol. The required equation is



Given



The required equation can be achieved by adding equations (a) and (b) and subtracting (c).



We know that

$$\Delta H^\ominus = \Delta U^\ominus + \Delta nRT$$

$$\text{or } \Delta U^\ominus = \Delta H^\ominus - \Delta nRT$$

$$\Delta n = (1 - 2) = -1, R = 2 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$$

$$\text{and } T = (25 + 273) = 298 \text{ K}$$

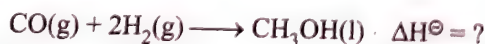
Substituting the values in above equation,

$$\Delta U^\ominus = -41.7 - (-1)(2 \times 10^{-3})(298)$$

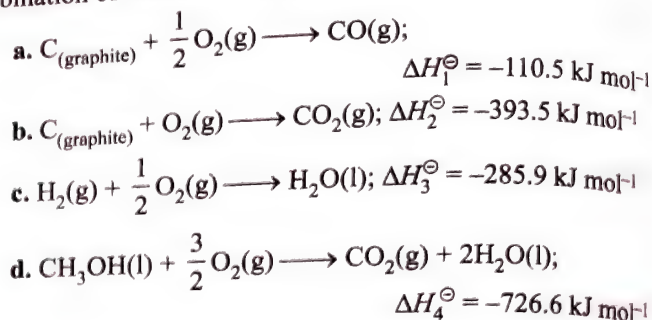
$$= -41.7 + 0.596 = -41.104 \text{ kcal}$$

ILLUSTRATION 6.53

Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst. The reaction is



Determine the enthalpy of this reaction by an appropriate combination of the following data:



Sol. The required equation can be obtained in the following manner:

$$\Delta H^\ominus = -\Delta H_1^\ominus + 2\Delta H_3^\ominus + \Delta H_2^\ominus - \Delta H_4^\ominus$$

$$\text{So, } \Delta H^\ominus = 110.5 - 571.8 - 393.5 + 726.6$$

$$= -128.2 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.54

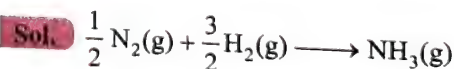
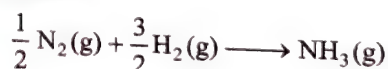
Standard heat of formation at 298 K is arbitrarily taken to be zero for

- Liquid bromine
- Gaseous bromine atoms
- Gaseous bromine molecules
- Solid bromine

Sol. a. Liquid bromine $[Br_2(l)]$ is standard state of bromine.

ILLUSTRATION 6.55

The standard heat of formation listed for gaseous NH_3 is $-11.00 \text{ kcal mol}^{-1}$ at 298 K. Given that at 298 K, the constant pressure heat capacities of gaseous N_2 , H_2 , and NH_3 are, respectively, 7.0, 6.0 and 8.0 cal mol^{-1} . Determine $\Delta H^\ominus_{298 \text{ K}}$ and $\Delta H^\ominus_{773 \text{ K}}$ for the reactions:



$$\Delta H^\ominus_{298 \text{ K}} = \sum_{f(P)} H^\ominus - \sum_{f(R)} H^\ominus = (-11.0 - 0) = -11.0 \text{ kcal mol}^{-1}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_2 - (-11.0)}{773 - 298} = \left(8.0 - \frac{1}{2} \times 7.0 - \frac{3}{2} \times 6.0 \right) \times 10^{-3}$$

$$\Delta H^\ominus_2 = -13.137 \text{ kcal mol}^{-1}$$

ILLUSTRATION 6.56

I. When ethyne is passed through a red hot tube, then formation of benzene takes place:

$$\Delta_f H^\ominus_{(C_2H_2)(g)} = 230 \text{ kJ mol}^{-1}$$

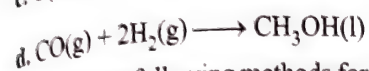
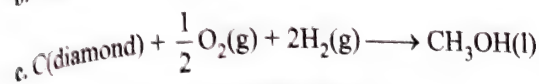
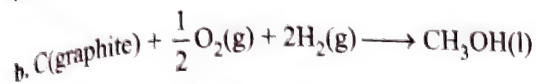
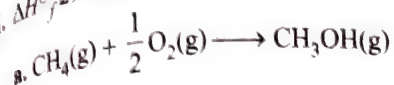
$$\Delta_f H^\ominus_{(C_6H_6)(g)} = 85 \text{ kJ mol}^{-1}$$

Calculate the standard heat of trimerisation of ethyne to benzene.



- a. 205 kJ mol⁻¹ b. 605 kJ mol⁻¹
c. -605 kJ mol⁻¹ d. -205 kJ mol⁻¹

II. ΔH_f^\ominus 298 K of methanol is given by the chemical equation



III. Which of the following methods for the calculation of heat of a reaction is not correct?

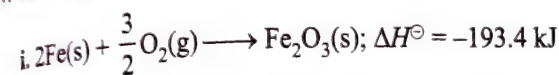
a. $\Delta H_{\text{reaction}}^\ominus = \sum \Delta_f H_{\text{products}}^\ominus - \sum \Delta_f H_{\text{reactants}}^\ominus$

b. $\Delta H_{\text{reaction}}^\ominus = \sum (\text{BE})_{\text{reactants}} - \sum (\text{BE})_{\text{products}}$

c. $\Delta H_{\text{reaction}}^\ominus = \sum \Delta_{\text{comb}} H_{\text{(reactants)}}^\ominus - \sum \Delta_{\text{comb}} H_{\text{(products)}}^\ominus$

d. $\Delta H_{\text{reaction}}^\ominus = \sum \Delta_{\text{solution}} H_{\text{(reactants)}}^\ominus - \sum \Delta_{\text{solution}} H_{\text{(products)}}^\ominus$

IV. Given:



What is ΔH^\ominus of the reaction?



- a. -227.2 kJ b. -272.3 kJ
c. 227.2 kJ d. 272.3 kJ



$$\Delta H^\ominus = -352.18 \text{ kJ}$$

Given heat of formation of HF, $\Delta_f H_{\text{(HF)}}^\ominus = -268.3 \text{ kJ}$

The heat of formation of HCl will be

- a. -22 kJ mol⁻¹ b. 88 kJ mol⁻¹
c. -92.21 kJ mol⁻¹ d. -183.8 kJ mol⁻¹

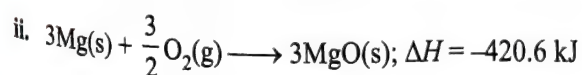
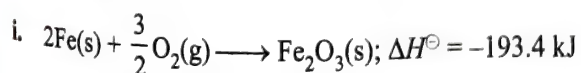
I. c.

$$\begin{aligned} [\Delta H_{\text{reaction}}^\ominus] &= \Delta_f H_{\text{(C}_6\text{H}_6)}^\ominus - 3\Delta_f H_{\text{(C}_2\text{H}_2)}^\ominus \\ &= 85 - 3(230) \\ &= -605 \text{ kJ} \end{aligned}$$

II. b. In the process of formation, the compound must be formed from constituent elements in their standard state.

III. d.

IV. a. Subtracting equation (i) from equation and (ii) multiplied by 3, we get



Subtracting (i) from (ii),



$$\Delta H^\ominus = -420.6 - (-193.4) = -227.2 \text{ kJ}$$

V. $\Delta H_{\text{reaction}}^\ominus = 2\Delta_f H_{\text{(HF)}}^\ominus - 2\Delta_f H_{\text{(HCl)}}^\ominus$

$$-352.18 = 2 \times (-268.3) - 2x$$

$$2x = 2(-268.3) + 352.18$$

$$x = -92.21 \text{ kJ mol}^{-1}$$

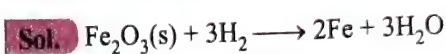
ILLUSTRATION 6.57

Calculate ΔH at 85°C for the reaction:



The data: $\Delta H_{298}^\ominus = -33.0 \text{ kJ mol}^{-1}$ and

Substance	$\text{Fe}_2\text{O}_3(\text{s})$	$\text{Fe}(\text{s})$	$\text{H}_2\text{O}(\text{l})$	$\text{H}_2(\text{g})$
$C_p^\ominus (\text{J K}^{-1} \text{ mol})$	103.0	25.0	75.0	28.0



$$\Delta C_p = (C_p)(\text{Product}) - (C_p)(\text{Reactant})$$

$$= (2 \times 25.0 + 3 \times 75.0) - (103.0 + 3 \times 28.0)$$

$$= 275.0 - 187.0 = 88.0 \text{ J}$$

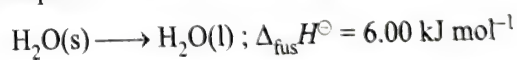
$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p$$

$$\frac{\Delta H_{558} - (-33.0)}{358 - 298} = 88.0 \times 10^{-3}$$

$$\Delta H_{358} = -27.72 \text{ kJ mol}^{-1}$$

6.10.2 ENTHALPY CHANGES DURING PHASE TRANSFORMATIONS

Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally, this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).



Here, $\Delta_{\text{fus}} H^\ominus$ is enthalpy of fusion in standard state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{\text{fus}} H^\ominus$.

Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires heat for evaporation. At constant temperature of its boiling point T_b and at constant pressure:



$\Delta_{\text{vap}} H^\ominus$ is the standard enthalpy of vaporisation.

Amount of heat required to vaporise one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its *standard enthalpy of vaporisation or molar enthalpy of vaporisation*, $\Delta_{\text{vap}} H^\ominus$.

Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimates at 195 K with $\Delta_{\text{sub}}H^\ominus = 25.2 \text{ kJ mol}^{-1}$; naphthalene sublimates slowly and for this $\Delta_{\text{sub}}H^\ominus = 73.0 \text{ kJ mol}^{-1}$.

Standard enthalpy of sublimation, $\Delta_{\text{sub}}H^\ominus$, is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1 bar).

The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transformations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mol of acetone than it does to vaporize 1 mol of water. Table 6.3 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

Table 6.3 Standard enthalpy changes of fusion and vaporisation

Substance	$T_f(\text{K})$	$\Delta_{\text{fus}}H^\ominus (\text{kJ mol}^{-1})$	$T_b(\text{K})$	$\Delta_{\text{vap}}H^\ominus (\text{kJ mol}^{-1})$
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl_4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

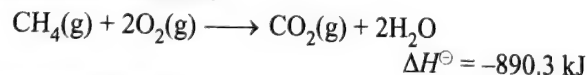
(T_f and T_b are melting and boiling points, respectively)

6.10.3 ENTHALPY OF COMBUSTION OR HEAT OF COMBUSTION ($\Delta_{\text{comb}}H^\ominus$)

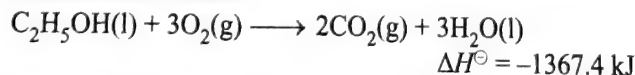
Enthalpy of combustion of a given compound is defined as the enthalpy change when one mole of this compound combines with the requisite amount of oxygen to given products in their stable forms. Combustion reactions are always accompanied by the evolution of heat, therefore, the value of $\Delta_c H$ is always negative.

For example,

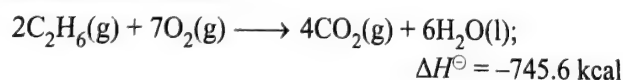
a. Combustion of methane



b. Combustion of ethanol



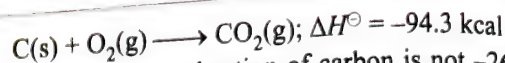
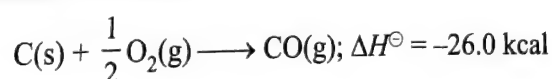
c. Combustion of ethane



Since 2 mol of C_2H_6 is involved, hence enthalpy of combustion of ethane

$$= -\frac{745.6}{2} = -372.8 \text{ kcal}$$

Combustion of carbon



The enthalpy of combustion of carbon is not -26.0 kcal as combustion is not complete because carbon monoxide can further be oxidised to carbon dioxide. The enthalpy of combustion of carbon is thus -94.3 kcal .

The enthalpies of combustion have a number of applications. Some of these are described below.

Calorific value of foods and fuels: Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas, etc., serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body. These substances undergo oxidation or combustion and release energy. These substances are, therefore, termed as fuels. An adult requires 2500 to 3000 kcal of energy per day. Since the values of enthalpies of combustion of different food articles are known, it becomes easy to calculate our daily requirements and thus select the articles of food so as to secure a balanced diet.

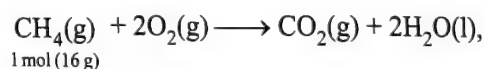
The grading of food articles and various fuels can be done on the basis of the values of enthalpies of combustion.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as calorific value.

Mathematically, *calorific value can be expressed as the amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised.*

$$\text{calorific value} = \frac{\text{Heat of combustion of fuel}}{\text{Atomic weight or molecular weight of the fuel}}$$

When methane burns, $890.3 \text{ kJ mol}^{-1}$ of energy is released.



$$\Delta H_{\text{CH}_4} = -890.3 \text{ kJ}$$

$$\text{So, the calorific value of methane} = -\frac{890.3}{16} = -55.6 \text{ kJ g}^{-1}$$

Table 6.4 Calorific values of some important foodstuffs and fuels

Fuel	Calorific value (kJ g^{-1})	Food	Calorific value (kJ g^{-1})
Wood	17	Milk	3.1
Charcoal	33	Egg	6.7
Kerosine	48	Rice	16.7
Methane	55	Sugar	17.3
LPG	55	Butter	30.4
Hydrogen	150	Ghee	37.6

Out of the fuels listed, hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel due to some technical problems. Of the various constituents of our food, fats and carbohydrates serve as the main sources of energy. The calorific value of proteins is quite low.

Measurement of ΔU and ΔH : Calorimetry

We can measure energy changes associated with chemical or physical by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter.

which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which the calorimeter is immersed as well as the heat capacity of the calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

- i. at constant volume, q_V
- ii. at constant pressure, q_P

ΔU measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Fig. 6.13). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change, i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_P by using the known heat capacity of the calorimeter.

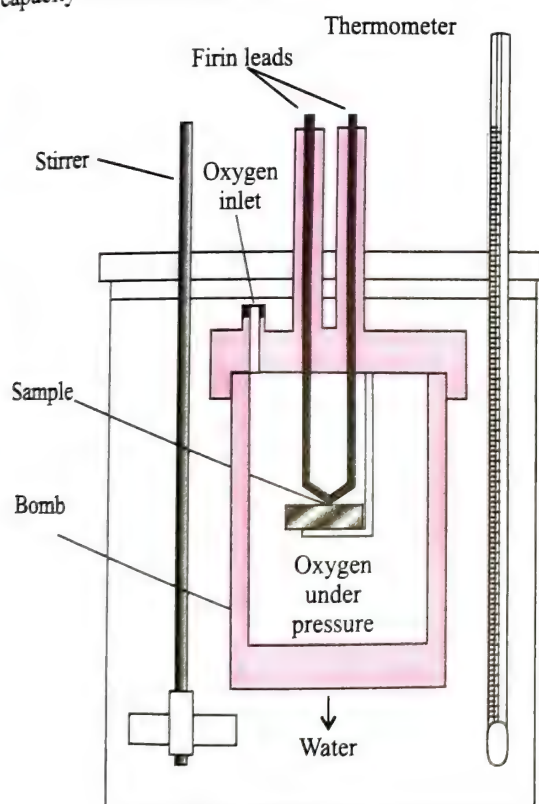


Fig. 6.13 Bomb calorimeter

ΔH measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig. 6.14. We know that $\Delta H = q_P$ (at constant P) and, therefore, heat absorbed or evolved, q_P at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_P will be negative and $\Delta_r H$ will also

be negative. Similarly in an endothermic reaction, heat is absorbed, q_P is positive, and therefore, $\Delta_r H$ will be positive.

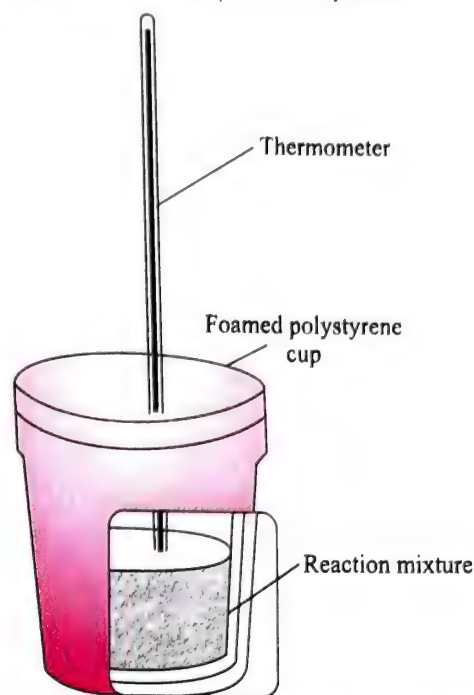


Fig. 6.14 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure)

Notes

1. Δ combustion H^\ominus is always negative.
2. There are certain reactions which involve combination with oxygen undergoing partial combustion and ΔH is +ve, e.g., $N_2 + O_2 \rightarrow 2NO$, $\Delta H = +ve$.
Again when F_2 combines with O_2 to form OF_2 , F_2 is reduced and not oxidized and ΔH for the reaction is +ve, i.e., $F_2 + \frac{1}{2}O_2 \rightarrow OF_2$, $\Delta H = +ve$.
3. The standard enthalpy of formation of graphite is taken as zero but of diamond it is not zero but is equal to $1.816 \text{ kJ mol}^{-1}$.
4. In a bomb calorimeter, $\Delta V = 0$.

Hence ΔH should be equal to ΔU . But this is not true.

This is because the relation, $\Delta H = \Delta U + P\Delta V$ holds good only at constant pressure.

$$H = U + PV$$

$$\text{or } \Delta H = \Delta U + P\Delta V + V\Delta P$$

$$\text{At constant pressure, } \Delta P = 0$$

$$\Delta H = \Delta U + P\Delta V$$

$$\text{At constant volume, } \Delta V = 0$$

$$\Delta H = \Delta U + V\Delta P$$

ILLUSTRATION 6.5B

The thermochemical equation for the combustion of ethylene gas, C_2H_4 , is



$$\Delta_r H^\ominus = -337 \text{ kcal}$$

Assuming 70% efficiency, calculate the weight of water at 20°C that can be converted into steam at 100°C by burning 1 m³ of C₂H₄ gas measured at STP. The heat of vaporisation of water at 20°C and 100°C are 1.00 kcal kg⁻¹ and 540 kcal kg⁻¹ respectively.

Sol. Number of moles in 1 m³ of ethylene = 44.6 mol

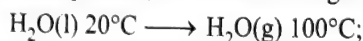
ΔH for 1 m³ of ethylene (44.6 mol of ethylene)

$$= n(C_2H_4) \times \Delta H(1 \text{ mole})$$

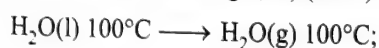
$$= -1.50 \times 10^4 \text{ kcal}$$

Therefore, the useful heat = $1.05 \times 10^4 \text{ cal}$

For the overall process, consider two stages:



$$\Delta H = C_p \Delta T = (1.00 \text{ kcal kg}^{-1}, K) (80 \text{ K}) = 80 \text{ kcal kg}^{-1}$$



$$\Delta H = 540 \text{ kcal kg}^{-1}$$

$$\therefore \Delta_{\text{total}} H = 620 \text{ kcal kg}^{-1}$$

Therefore, weight of water converted into steam

$$= \frac{\text{Amount of heat available}}{\text{Heat required/kg}} = \frac{1.05 \times 10^4}{620} = 16.9 \text{ kg}$$

ILLUSTRATION 6.59

The heat of combustion of glycogen is about 476 kJ mol⁻¹ of carbon. Assume that average heat loss by an adult male is 150 W. If we were to assume that all the heat comes from oxidation of glycogen, how many units of glycogen (1 mol carbon per unit) must be oxidised per day to provide for this heat loss?

Sol. Total energy required in the day

$$= \frac{150 \times 24 \times 60 \times 60}{1000} \text{ kJ} = 12960 \text{ kJ} \quad (1 \text{ watt} = J s^{-1})$$

$$\text{Units of glycogen required} = \frac{12960}{476} = 27.22 \text{ units}$$

ILLUSTRATION 6.60

The temperature of a bomb calorimeter was found to rise by 1.617 K when a current of 3.20 A was passed for 27 s from a 12 V source. Calculate the calorimeter constant.

Sol. Energy absorbed by the calorimeter

$$= I \times t \times V = 3.2 \times 27 \times 12 = 1036.8 \text{ J}$$

Calorimeter constant (ms) can be calculated as,

$$q = ms \Delta t$$

$$1036.8 = ms \times 1.617$$

$$ms = 641.187 \text{ kJ}$$

ILLUSTRATION 6.61

Assume that for a domestic hot water supply 150 kg of water per day must be heated from 10°C to 65°C and gaseous fuel propane C₃H₈ is used for this purpose. What moles and volume of propane (in L at STP) would have to be used for heating domestic water, ΔH for combustion of propane is -2050 kJ mol⁻¹ and specific heat of water is $4.184 \times 10^{-3} \text{ kJ g}^{-1}$.

Sol. Heat taken up by water = $ms \Delta T$

$$= 150 \times 103 \times 4.184 \times 10^{-3} \times 55 = 34518 \text{ kJ}$$

2050 kJ heat is provided by 1 mol C₃H₈

Therefore, 34518 kJ heat is provided by 34518/2050

$$= 16.838 \text{ mol of } C_3H_8$$

Therefore, volume of C₃H₈ at NTP

$$= 16.838 \times 22.4 \text{ L} = 377.17 \text{ L}$$

ILLUSTRATION 6.62

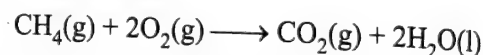
A sample of 0.16 g CH₄ was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (a) constant volume and (b) constant pressure. The thermal capacity of calorimeter system is 17.0 kJ K⁻¹ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Sol. Heat of combustion at constant volume, ΔU

$$= \text{Heat capacity of calorimeter system} \times \text{Rise in temperature} \times \frac{\text{Molecular mass of compound}}{\text{Mass of compound}}$$

$$= 17.0 \times 0.5 \times \frac{16}{0.16} = 850$$

$$\text{i.e., } \Delta U = -850 \text{ kJ mol}^{-1}$$



$$\Delta n = 1 - 3 = -2, T = 300 \text{ K}, R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta H^\ominus = \Delta U^\ominus + \Delta nRT$$

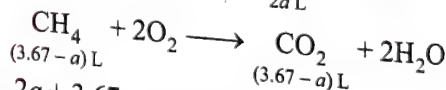
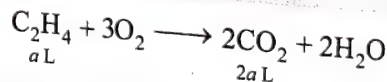
$$= -850 + (-2) \times 8.314 \times 10^{-3} \times 300$$

$$= -850 - 4.988 = -854.988 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.63

A gas mixture of 3.67 L of ethylene and methane on complete combustion at 25°C produces 6.11 L of CO₂. Find out the heat evolved on burning 1 L of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol⁻¹, respectively, at 25°C.

Sol.



$$\text{Given, } 2a + 3.67 - a = 6.11$$

$$a = 2.44 \text{ L}$$

Volume of ethylene in mixture = 2.44 L

Volume of methane in mixture = 1.23 L

$$\text{Volume of ethylene in 1 L mixture} = \frac{2.44}{3.67} = 0.6649 \text{ L}$$

$$\text{Volume of methane in 1 L mixture} = \frac{1.23}{3.67} = 0.3351 \text{ L}$$

24.45 L of a gas at 25°C correspond to 1 mol.

Thus, heat evolved by burning 0.6649 L of ethylene

$$= -\frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

and heat evolved by burning 0.3351 L of methane

$$= -\frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So, total heat evolved by burning 1 L of mixture

$$= -38.69 - 12.21$$

$$= -50.90 \text{ kJ}$$

ILLUSTRATION 6.64

The heat of combustion of $\text{CH}_4(\text{g})$, $\text{C}_2\text{H}_6(\text{g})$, and $\text{H}_2(\text{g})$ are 890.3, 1559.7, and 285.9 kJ mol^{-1} , respectively. Which of these fuels is most efficient?

Sol. Fuel efficiency $\eta_{\text{CH}_4} = \frac{890.3}{16} = \frac{\text{Heat evolved}}{\text{Molecular weight}}$
 $= 55.64 \text{ kJ}$

$$\eta_{\text{C}_2\text{H}_6} = \frac{1559.7}{30} = 51.99 \text{ kJ}$$

$$\text{and } \eta_{\text{H}_2} = \frac{285.9}{2} = 142.95 \text{ kJ}$$

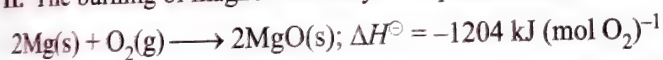
Hence, $\text{H}_2(\text{g})$ is the best fuel.

ILLUSTRATION 6.65

I. Select the correct statement from the following:

- In exothermic reaction, the value of equilibrium constant increases with rise of temperature.
- In endothermic reaction, the value of equilibrium constant decreases with rise in temperature.
- In exothermic reaction, the value of equilibrium constant decreases with rise of temperature.
- In endothermic reaction, the value of equilibrium constant remains constant with rise of temperature.

II. The burning of magnesium may be represented by:



Which one of the following correctly describe what would happen if the reaction were allowed to proceed at constant external pressure in such a way that no energy transfer could take place between the reaction mixture and its surroundings?

- No reaction could occur.
- The temperature of the reaction mixture would increase.
- The temperature of the reaction mixture would decrease.
- The pressure of the system would increase.

Sol.

I. c. During exothermic reaction, heat evolved on reaction proceeding forward direction. When the temperature increases of the system the reaction will proceed in backward direction.

II. b. In combustion, heat evolved, hence temperature of system will increase.

ILLUSTRATION 6.66

A natural gas may be assumed to be a mixture of methane and ethane only. On complete combustion of 10 L of gas at STP the heat evolved was 474.6 kJ. Assuming $\Delta_{\text{comb}} H^\ominus \text{CH}_4(\text{g}) = -894 \text{ kJ mol}^{-1}$ and $\Delta_{\text{comb}} H^\ominus \text{C}_2\text{H}_6 = -1500 \text{ kJ}$. Calculate the percentage composition of the mixture by volume.

Sol.

$$x \text{ L} \longrightarrow \text{CH}_4; \text{mole of CH}_4 = x/22.4$$

$$(10 - x) \text{ L} \longrightarrow \text{C}_2\text{H}_6; \text{mole of C}_2\text{H}_6 = (10 - x)/22.4$$

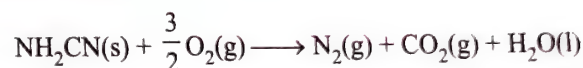
$$\text{Heat evolved} = \frac{x}{22.4} \times 894 + \frac{(10 - x)}{22.4} \times 1500$$

$$474.6 = \frac{x}{22.4} \times 894 + \frac{(10 - x)}{22.4} \times 1500$$

$$x = 0.745, \% \text{CH}_4 = 74.5\%$$

ILLUSTRATION 6.67

I. The reaction:



was carried out in a bomb calorimeter. The heat released was 743 kJ mol^{-1} . The value of $\Delta H_{300 \text{ K}}$ for this reaction would be

- 740.5 kJ mol^{-1}
- 741.75 kJ mol^{-1}
- 743.0 kJ mol^{-1}
- 744.25 kJ mol^{-1}

II. The value of $\Delta H_{\text{O-H}}$ is 109 kcal mol^{-1} . Then formation of one mole of water in gaseous state from $\text{H}(\text{g})$ and $\text{O}(\text{g})$ is accompanied by

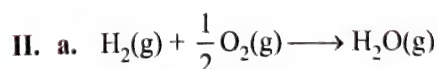
- Release of 218 kcal of energy
- Release of 109 kcal of energy
- Absorption of 218 kcal of energy
- Unpredictable

III. In the reversible reaction of the type $A + B \rightleftharpoons AB$, in general.

- Neither of the reactions will be endothermic.
- Both forward and backward reactions are exothermic.
- Forward reaction will be exothermic.
- Backward reaction will be exothermic.

Sol.

I. b.



$$\Delta H = -(2 \times \Delta_{\text{O-H}} H^\ominus)$$

$$\Delta H = -2 \times 109 = -218 \text{ kcal}$$

III. c. As in the formation of new bonds, energy releases. Therefore, the forward reaction will be exothermic.

ILLUSTRATION 6.68

I. Which of the following expressions is true?

$$\text{a. } \Delta_f H^\ominus(\text{CO}, \text{g}) = \frac{1}{2} \Delta_f H^\ominus(\text{CO}_2, \text{g})$$

$$b. \Delta_f H^\ominus(\text{CO}, g) = \Delta_f H^\ominus(\text{C, graphite}) = \frac{1}{2} \Delta_f H^\ominus(\text{O}_2, g)$$

$$c. \Delta_f H^\ominus(\text{CO}, g) = \Delta_f H^\ominus(\text{CO}_2, g) - \frac{1}{2} \Delta_f H^\ominus(\text{O}_2, g)$$

$$d. \Delta_f H^\ominus(\text{CO}, g) = \Delta_{\text{comb}} H^\ominus(\text{C, graphite}) - \Delta_{\text{comb}} H^\ominus(\text{CO}, g)$$

II. The heat of combustion of solid benzoic acid at constant volume is -321.30 kJ at 27°C . The heat of combustion at constant pressure is

$$a. -321.30 - 300R$$

$$b. -321.30 + 300R$$

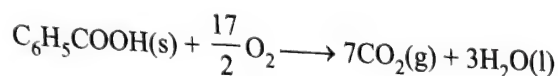
$$c. -321.30 - 450R$$

$$d. -321.30 + 900R$$

Sol.

I. d.

$$\text{II. c. } \Delta H^\ominus = \Delta U^\ominus + \Delta nRT$$



$$\Delta n = n_p - n_R = 7 - \frac{17}{2} = \frac{-3}{2}$$

$$\therefore \Delta H^\ominus = -321.30 + \left[\frac{-3}{2} \times 300 \text{ K} \times R \right]$$

$$= -321.30 - 450R$$

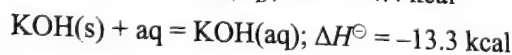
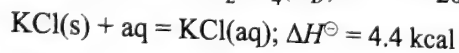
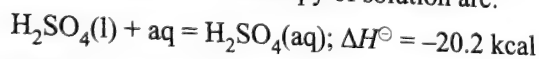
6.10.4 ENTHALPY OF SOLUTION ($\Delta_{\text{sol}} H^\ominus$)

It is the enthalpy change when 1 mole of solute is dissolved in large excess of a solvent so that further addition of solvent does not produce any more heat change.

It may be noted that the enthalpy change when 1 mole of solute is dissolved in a definite quantity or moles of solvent is called integral enthalpy of solution, whereas the enthalpy change observed by dissolving 1 mol of solute in infinite amount of solvent so that the interaction between solute molecules are negligible is called *enthalpy of solution* or more specifically, the *differential enthalpy of solution*.

If water is the solvent, then the symbol 'aq' (aqueous) is used to represent large or infinite dilutions.

Some examples of enthalpy of solution are:



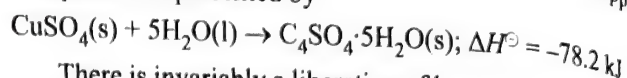
Enthalpy of ideal solution is taken zero.

Generally, dissolution of substances in a solvent is a disintegration process. This process needs energy. In such cases, energy is absorbed, i.e., ΔH is positive. But in some cases, besides the process of breaking or ionisation, there is hydrate formation. During hydration heat is evolved. The net result is that heat is either evolved or absorbed. There are also cases in which heat of separation of ions is just equal to the heat of hydration and there is very little heat effect as in the case of sodium chloride. The heat of solution of NaCl is very small as the heat of ionisation is nearly equal to the heat of hydration.

6.10.5 ENTHALPY OF HYDRATION ($\Delta_{\text{hyd}} H^\ominus$)

a. Enthalpy of hydration of an anhydrous or partially hydrated salt is defined as the enthalpy change when one mole of it combine with requisite amount of water to form a new hydrated stable salt.

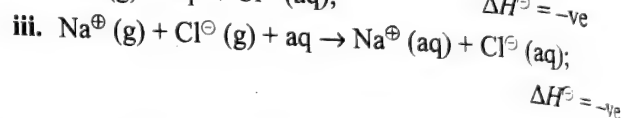
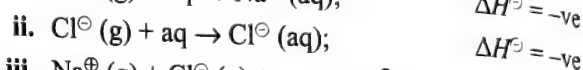
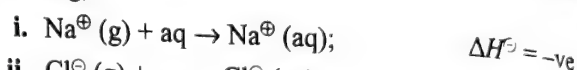
For example, enthalpy of hydration of anhydrous copper sulphate is represented by



There is invariably a liberation of heat in such reactions, i.e., the value of ΔH is negative.

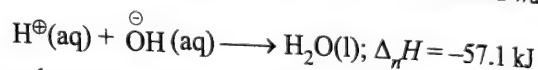
b. Enthalpy of Hydration ($\Delta_{\text{hyd}} H^\ominus$)

It is also defined as the enthalpy change (released) when one mole of a compound in its constituent gaseous ions is dissolved in aqueous water to give their constituent aqueous ions, eg,



6.10.6 ENTHALPY OF NEUTRALISATION ($\Delta_n H^\ominus$)

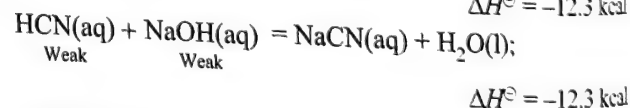
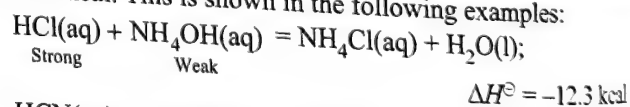
The enthalpy of neutralisation is defined as the enthalpy change when one of equivalent of H^+ in dilute solution combines with one of equivalent of OH^- to give rise to undissociated water, i.e.,



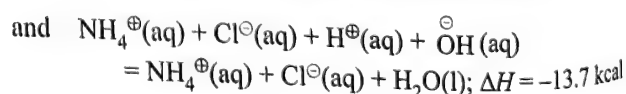
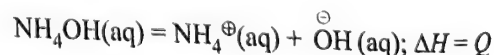
In such reactions, there is always a release of heat because of the bond formation $\text{H}-\text{OH}$, i.e., ΔH is negative.

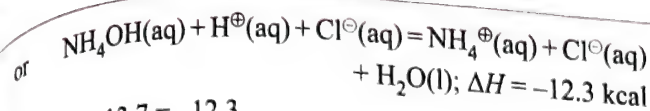
Whenever one mole of a strong monoprotic acid (HCl , HNO_3) is mixed with the one mole of a strong base (NaOH , KOH), the above neutralisation reaction takes place, since these acids and bases are present in the completely dissociated form in dilute solutions. The corresponding enthalpy change is of the order of -57.1 kJ or -13.7 kcal .

However, when a strong acid and a weak base or a weak acid and a strong base or a weak acid and a weak base are mixed in equivalent amounts the heat evolved or change in enthalpy is less than 13.7 kcal . This is shown in the following examples:



The reason for the lower value is that part of the heat energy evolved is utilised in the complete ionisation of a weak acid or a weak base or both. Hence, the net heat of neutralisation is less than 13.7 kcal . The neutralisation of NH_4OH with HCl can be explained in the following way:





So $Q - 13.7 = -12.3$

or $Q = 13.7 - 12.3 = 1.4 \text{ kcal}$

Hence, 1.4 kcal of heat energy is absorbed for ionisation of NH_4OH which get subtracted from 13.7 kcal. Thus, the observed value of heat of neutralisation is not -13.7 kcal but 12.3 kcal.

Note:
1. The absolute value of heat of neutralisation of HF is more than 57.1 kJ (i.e., 68 kJ). This is due to very high heat of hydration of F^- ion.

QUESTION BASED ON ENTHALPY OF NEUTRALISATION ($\Delta_n H^\ominus$)

ILLUSTRATION 6.69

I. Calculate the enthalpy change when 50 mL of 0.01 M $\text{Ca}(\text{OH})_2$ reacts with 25 mL of 0.01 M HCl. Given that ΔH^\ominus neutralisation of strong acid and strong base is 140 kcal mol^{-1} .

- a. 14 kcal b. 35 cal c. 10 cal d. 7.5 cal

II. Equal volumes of 1 M HCl and 1 M H_2SO_4 are neutralised by 1 M NaOH solution and x and y kJ/equivalent of heat are liberated, respectively. Which of the following relations is correct?

- a. $x = 2y$ b. $x = 3y$ c. $x = 4y$ d. $x = \frac{1}{2}y$

III. Which of the following acid will release maximum amount of heat when completely neutralised by strong base NaOH?

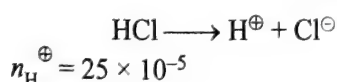
- a. 1 M HCl b. 1 M HNO_3
c. 1 M HClO_4 d. 1 M H_2SO_4

IV. The enthalpy of neutralisation of a strong acid by a strong base is $-57.32 \text{ kJ mol}^{-1}$. The enthalpy of formation of water is $-285.84 \text{ kJ mol}^{-1}$. The enthalpy of formation of hydroxyl ion is

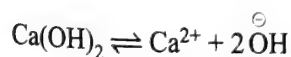
- a. $+228.52 \text{ kJ mol}^{-1}$ b. $-114.26 \text{ kJ mol}^{-1}$
c. $-228.52 \text{ kJ mol}^{-1}$ d. $+114.2 \text{ kJ mol}^{-1}$

Sol.

I. b. Number of moles of HCl = $\frac{MV}{1000} = \frac{0.01 \times 25}{1000} = 25 \times 10^{-5}$



Number of moles of $\text{Ca}(\text{OH})_2 = \frac{MV}{1000} = \frac{0.01 \times 50}{1000} = 50 \times 10^{-5}$



$$n_{\text{OH}^-} = 2 \times 50 \times 10^{-5} = 10^{-3}$$

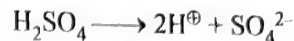
In the process of neutralisation, 25×10^{-5} mole H^+ will be completely neutralised.

$$\therefore \Delta H^\ominus = 140 \times 25 \times 10^{-5} \text{ kcal} = 0.035 \text{ kcal} = 35 \text{ cal}$$

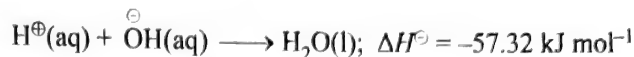
II. d. Since, H_2SO_4 gives 2 moles H^+ , HCl gives 1 mole H^+ from 1 mole after ionisation. Hence, H_2SO_4 will release double amount of heat as compared to HCl.

$$\text{i.e., } y = 2x \text{ or } x = \frac{y}{2}$$

III. d. Ionisation of H_2SO_4 gives double amount of H^+ ions as compared to other acids.



IV. The process of neutralisation is



$$\Delta H^\ominus_{\text{reaction}} = \Sigma \text{Heat of formation of products}$$

$$- \Sigma \text{Heat of formation of reactants}$$

$$= \Delta_f H^\ominus_{\text{H}_2\text{O}(\text{l})} - (\Delta_f H^\ominus_{\text{H}^+(\text{aq})} + \Delta_f H^\ominus_{\text{OH}^-(\text{aq})})$$

$$-57.32 = -285.84 - (0 + x)$$

$$x = -285.84 + 57.32 = -228.52 \text{ kJ}$$

Thus, the enthalpy of formation of hydroxyl ion is -228.52 kJ .

ILLUSTRATION 6.70

What would be the heat released when:

- a. 0.5 mol of HCl is neutralised with 0.5 mol of NaOH
b. 0.5 mol of HNO_3 is neutralised with 0.3 mol of NaOH
c. 100 mL of 0.2 M HCl + 200 mL 0.2 M KOH
d. 200 mL of 0.1 M H_2SO_4 + 150 mL of 0.2 M KOH

Sol.

a. 0.5 mol of HCl is neutralised by 0.5 mol of NaOH

$$\therefore \Delta H = -57.1 \times 0.5 = -28.55 \text{ kJ}$$

b. 0.3 mol of HNO_3 will neutralise 0.3 mol of NaOH.

$$\therefore \Delta H = -57.1 \times 0.3 = -17.1 \text{ kJ}$$

c. $\text{HCl} = 100 \times 0.2 = 20 \text{ mmol}$ or 20 mEq

$$\text{KOH} = 200 \times 0.2 = 40 \text{ mmol}$$
 or 40 mEq

$$\therefore 20 \text{ mEq will neutralise}$$

$$\text{or } 20 \times 10^{-3} \text{ Eq will neutralise}$$

$$\Delta H = (-57.1 \times 20 \times 10^{-3}) = -1.14 \text{ kJ}$$

d. $\text{H}_2\text{SO}_4 = 200 \times 0.1 \times 2$ (since H_2SO_4 is dibasic)

$$= 40 \text{ mEq}$$

$$\text{KOH} = 150 \times 0.2 = 30 \text{ mEq}$$

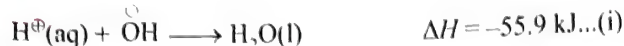
$$\therefore 30 \text{ mEq or } 30 \times 10^{-3} \text{ Eq will neutralise}$$

$$\therefore \Delta H = -57.1 \times 30 \times 10^{-3} = -1.713 \text{ kJ}$$

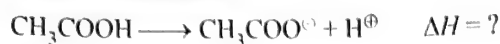
ILLUSTRATION 6.71

Enthalpy of neutralisation of acetic acid by NaOH is $-50.6 \text{ kJ mol}^{-1}$. Calculate ΔH for ionisation of CH_3COOH . Given, the heat of neutralisation of a strong acid with a strong base is $-55.9 \text{ kJ mol}^{-1}$.

Sol. The neutralisation of a strong acid by a strong base is represented by:



We have to calculate:



Given:



Subtract equation (i) from equation (ii), we get

$$\begin{aligned} \Delta H &= \Delta H_2 - \Delta H_1 \\ &= -50.6 - (-55.9) = 5.3 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.72

A constant pressure calorimeter consists of an insulated beaker of mass 92 g made up of glass with heat capacity $0.75 \text{ J K}^{-1} \text{ g}^{-1}$. The beaker contains 100 mL of 1 M HCl at 22.6°C to which 100 mL of 1 M NaOH at 23.4°C is added. The final temperature after the reaction is complete is 29.3°C . What is ΔH per mole for this neutralization reaction? Assume that the heat capacities of all solutions are equal that of same volumes of water.

Sol. Initial average temperature of the acid and base

$$= \frac{22.6 + 23.4}{2} = 23.0^\circ\text{C}$$

$$\text{Rise in temperature} = (29.3 - 23.0) = 6.3^\circ\text{C}$$

$$\begin{aligned} \text{Total heat produced} &= (m_1 S_1 + m_2 S_2) \Delta t \\ &= (92 \times 0.75 + 200 \times 4.184) \times 6.3 \\ &= (905.8) \times 6.3 = 5706.54 \text{ J} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of neutralisation} &= -\frac{5706.54}{100} \times 1000 \times 1 \\ &= -57065.4 \text{ J} \approx -57 \text{ kJ} \end{aligned}$$

ILLUSTRATION 6.73

150 mL of 0.5 N nitric acid solution at 25.35°C was mixed with 150 mL of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C . Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Sol. Total mass of solution = $150 + 100 = 300 \text{ g}$

$$\begin{aligned} Q &= \text{Total heat produced} = 300 \times (28.77 - 25.35) \text{ cal} \\ &= 300 \times 3.42 = 1026 \text{ cal} \end{aligned}$$

$$\begin{aligned} \text{Heat of neutralisation} &= \frac{Q}{150} \times 1000 \times \frac{1}{0.5} \\ &= \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal} \end{aligned}$$

Since heat is liberated, heat of neutralisation should be negative.

So, heat of neutralisation = -13.68 kcal

ILLUSTRATION 6.74

I. The enthalpy change ΔH for the neutralisation of 1 M HCl by caustic potash in dilute solution at 298 K is
a. 68 kJ b. 65 kJ c. 57.3 kJ d. 50 kJ

II. Enthalpy of neutralisation of the reaction between $\text{CH}_3\text{COOH}(\text{aq})$ and $\text{NaOH}(\text{aq})$ is $-13.2 \text{ kcal Eq}^{-1}$ and that of the reaction between $\text{H}_2\text{SO}_4(\text{aq})$ and $\text{KOH}(\text{aq})$ is $-13.7 \text{ kcal Eq}^{-1}$. The enthalpy of dissociation of $\text{CH}_3\text{COOH}(\text{aq})$ is
a. $-0.5 \text{ kcal Eq}^{-1}$ b. $+0.5 \text{ kcal Eq}^{-1}$
c. $-26.9 \text{ kcal Eq}^{-1}$ d. $+13.45 \text{ kcal Eq}^{-1}$

Sol.

- I. c. Since, both HCl and KOH are strong, 57.3 kJ heat will be released.
- II. b. Dissociation enthalpy of $\text{CH}_3\text{COOH} = 13.7 - 13.2 = 0.5 \text{ kcal Eq}^{-1}$. Thus, 0.5 kcal Eq^{-1} heat will be used to dissociate CH_3COOH completely.

ILLUSTRATION 6.75

When a student mixed 50 mL of 1 M HCl and 150 mL of 1 M NaOH in a coffee cup calorimeter, the temperature of the resultant solution increases from 21°C to 27.5°C . Assuming that the calorimeter absorbs only a negligible quantity of heat, that the total volume of solution is 100 mL, its density 1 g mL^{-1} and that its specific heat is 4.18 J g^{-1} . Calculate:

- a. The heat change during mixing.
b. The enthalpy change for the reaction
 $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{aq})$

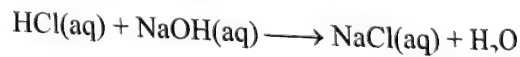
Sol. Number of moles of HCl and NaOH added

$$= \frac{MV}{1000} = \frac{1 \times 150}{1000} = 0.15$$

$$\text{Mass of mixture} = V \times d = 1000 \times 1 = 100 \text{ g}$$

$$\begin{aligned} \text{Heat evolved, } q &= ms \Delta T = 100 \times 4.18 \times (27.5 - 21.0) \\ &= 100 \times 4.18 \times 6.5 \text{ J} = 2717 \text{ J} = 2.717 \text{ kJ} \end{aligned}$$

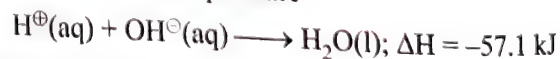
The involved reaction is



$$\Delta H^\ominus = \text{Heat evolved per mol} = \frac{-2.717}{0.15} = -18.11 \text{ kJ}$$

ILLUSTRATION 6.76

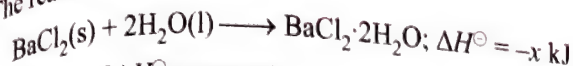
I. At a particular temperature



The approximate heat evolved when 400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution will be

- a. 3.426 kJ b. 13.7 kJ
c. 5.2 kJ d. 55 kJ

II. The reaction given below



The value of ΔH^\ominus represents

- a. Enthalpy of hydration b. Enthalpy of solution
c. Enthalpy of dilution d. None of the above

III. The heats evolved in combustion of rhombic and monoclinic sulphur are, respectively, 70960 and 71030 cal mol⁻¹. What will be the heat of conversion of rhombic sulphur to monoclinic?

- a. 70960 cal b. 71030 cal
c. -70 cal d. +70 cal

IV. If the enthalpy of combustion of C(graphite) is -393.3 kJ mol⁻¹, then for producing 39.3 kJ of heat the amount of carbon required is

- a. 1.5 mol b. 0.5 mol c. 1.2 g d. 12 mg

Sol.

I. a. Number of equivalent of H₂SO₄ taken

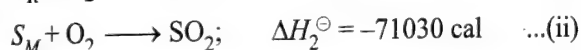
$$= \frac{0.2 \times 2 \times 400}{1000} = 0.16$$

$$\text{Number of equivalent of KOH added} = \frac{600 \times 0.1}{1000} = 0.06$$

Number of equivalents of acids and bases which neutralized each other = 0.06

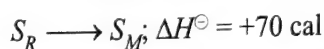
$$\therefore \text{Heat evolved} = 0.06 \times 57.1 \text{ kJ} = 3.426 \text{ kJ}$$

II. a. Enthalpy of hydration.



Subtracting equation (ii) from equation (i), we get

$$\begin{aligned} \Delta H^\ominus &= \Delta H_1^\ominus - \Delta H_2^\ominus \\ &= -70960 - (-71030) = +70 \text{ cal.} \end{aligned}$$



IV. c. 393.3 kJ energy produced by 12 g C

$$\text{Therefore, 39.3 kJ energy produced by } \frac{12 \times 39.3}{393.3}$$

$$= 1.2 \text{ g of C(graphite)}$$

ILLUSTRATION 6.77

I. Given $\Delta_f H^\ominus(\text{HCN}) = 45.2 \text{ kJ mol}^{-1}$ and $\Delta_f H^\ominus(\text{CH}_3\text{COOH}) = 2.1 \text{ kJ mol}^{-1}$. Which one of the following facts is true?

- a. $pK_a(\text{HCN}) = pK_a(\text{CH}_3\text{COOH})$
b. $pK_a(\text{HCN}) > pK_a(\text{CH}_3\text{COOH})$
c. $pK_a(\text{HCN}) < pK_a(\text{CH}_3\text{COOH})$
d. $pK_a(\text{HCN}) = (45.17/2.07) pK_a(\text{CH}_3\text{COOH})$

II. The heat of neutralisation of aqueous hydrochloric acid by NaOH is $x \text{ kcal mol}^{-1}$ of HCl. Calculate the heat of neutralisation per mol of aqueous acetic acid.

- a. $0.5x \text{ kcal}$

b. $x \text{ kcal}$

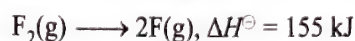
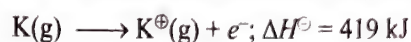
c. $2x \text{ kcal}$

d. Cannot be calculated from the given data

III. Under the same conditions, how many mL of 1 M KOH and 0.5 M H₂SO₄ solutions, respectively, when mixed to form a total volume of 100 mL, produces the highest rise in temperature?

- a. 67, 33 b. 33, 67 c. 40, 60 d. 50, 50

IV. Given: The heat of sublimation of K(s) is 89 kJ mol⁻¹.



The lattice energy of KF(s) is -813 kJ mol⁻¹, the heat of formation of KF(s) is -563 kJ mol⁻¹. The E_A of F(g) is

- a. -413 b. -336 c. -1149 d. +413

Sol.

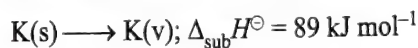
I. b. $pK_a(\text{HCN}) > pK_a(\text{CH}_3\text{COOH})$

II. d. It cannot be determined.

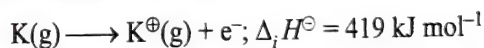
III. d. 50, 50 because H₂SO₄ is diprotic acid. It liberates 2H⁺ per mole of acid.

IV. b. Given that:

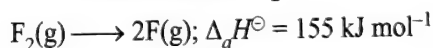
Heat of sublimation of K(s)



Heat of ionisation



Heat of atomisation of F₂



Lattice energy $\Delta_L H^\ominus = -813 \text{ kJ mol}^{-1}$

Heat of formation $\Delta_f H^\ominus = -563 \text{ kJ mol}^{-1}$

[Heat of electron affinity of F(g) = ?]

$$\therefore \Delta_f H^\ominus = \Delta_{\text{sub}} H^\ominus + \Delta_{\text{ie}} H^\ominus + \frac{1}{2} \Delta_a H^\ominus + \Delta_{\text{Et}} H^\ominus + \Delta_i H^\ominus$$

$$\text{or } \Delta_{\text{EA}} H^\ominus = \Delta_f H^\ominus - \Delta_{\text{sub}} H^\ominus - \Delta_i H^\ominus - \frac{1}{2} \Delta_a H^\ominus - \Delta_L H^\ominus$$

Substituting all the values:

$$\begin{aligned} \Delta_{\text{EA}} H^\ominus &= -563 - 89 - 419 - \frac{155}{2} + 813.0 \\ &\approx -336 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.78

I. If the heat of dissolution of anhydrous CuSO₄ and CuSO₄·5H₂O is -15.89 kcal and 2.80 kcal, respectively, then the heat of hydration of CuSO₄ to form CuSO₄·5H₂O is

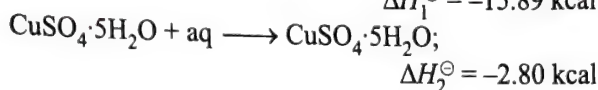
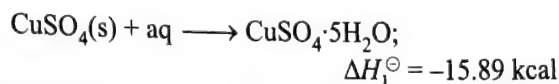
- a. -13.09 kcal b. -18.69 kcal
c. +13.09 kcal d. +18.69 kcal

- II. One mole of anhydrous AB dissolves in water and liberates 21.0 J mol^{-1} of heat. The value of ΔH^\ominus (hydration) of AB is -29.4 J mol^{-1} . The heat of dissolution of hydrated salt $\text{AB} \cdot 2\text{H}_2\text{O}(\text{s})$ is

- a. 50.4 J mol^{-1} b. 8.4 J mol^{-1}
c. -50.4 J mol^{-1} d. -8.4 J mol^{-1}

Sol.

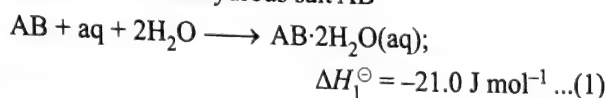
I. b.



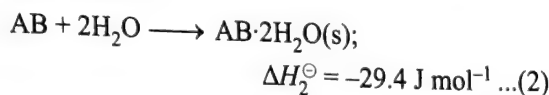
$$\Delta_{\text{hyd}} H^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus$$

$$\text{Heat of hydration} = -15.89 - 2.80 = -18.69 \text{ kcal}$$

- II. b. Dissolution of anhydrous salt AB

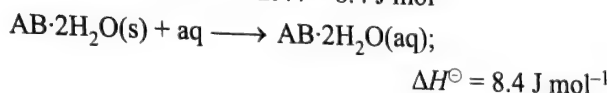


Hydration of AB salt



Subtracting equation (2) from (1) we get

$$\Delta_{\text{hyd}} H^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus = -21.0 + 29.4 = 8.4 \text{ J mol}^{-1}$$



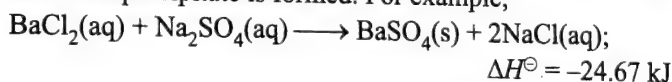
6.10.7 ENTHALPY OF TRANSITION (ΔH^\ominus)

Enthalpy of transition is defined as the enthalpy change when one mole of one allotropic form changes to another. For example,



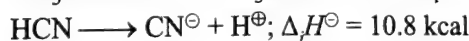
6.10.8 ENTHALPY OF PRECIPITATION

Enthalpy of precipitation is defined as the enthalpy change when one mole of a precipitate is formed. For example,



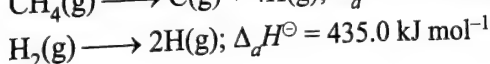
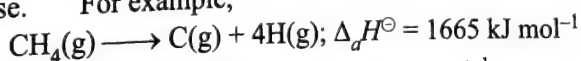
6.10.9 ENTHALPY OF IONISATION ($\Delta_i H^\ominus$)

Enthalpy of ionisation is defined as the enthalpy change when one mole of an electrolyte completely dissociates into ions. For example,



6.10.10 ENTHALPY OF ATOMISATION ($\Delta_a H^\ominus$)

Enthalpy of atomisation is defined as the enthalpy change when breaking one mole of bonds completely to obtain atoms in the gas phase. For example,

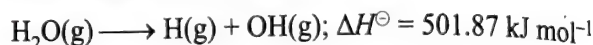


6.10.11 BOND ENTHALPY ($\Delta_{\text{bond}} H^\ominus$)

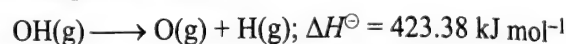
Bond enthalpy of a given bond is defined as the average enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state.

The term bond enthalpy may be distinguished from the term bond dissociation enthalpy which is defined as the enthalpy required to dissociate a given bond of some specific compound. For example, say of the O—H bond. The enthalpy of dissociation of the O—H bond depends on the nature of the molecular species from which the H atom is being separated.

For example, in water molecule



However, to break the O—H bond in the hydroxy requires a different quantity of heat



The bond enthalpy, $\Delta_{\text{bond}} H^\ominus$, is defined as the average of these two values, that is

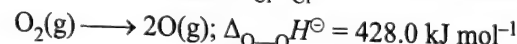
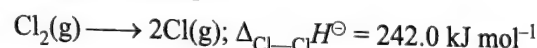
$$\Delta_{\text{bond}} H^\ominus = \frac{501.87 \text{ kJ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

In a diatomic molecule, the bond dissociation energy is same as bond enthalpy. For example, the energy required to break one mol of H—H bonds in gaseous state is $435.0 \text{ kJ mol}^{-1}$. Therefore, the bond enthalpy of H—H bond is $435.0 \text{ kJ mol}^{-1}$.

This may be expressed as:

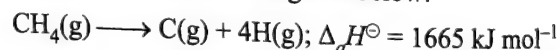
$$\Delta_{\text{H-H}} H^\ominus = 435.0 \text{ kJ mol}^{-1}$$

It is quite clear that dissociation of H_2 molecule leads to the formation of gaseous atoms. Therefore, this is also known as the enthalpy of atomisation ($\Delta_a H^\ominus$). This is true for all diatomic molecules. For example:

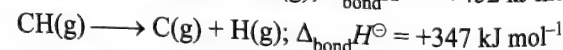
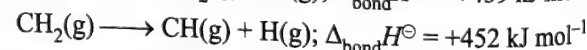
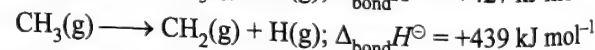
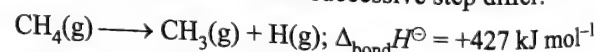


In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

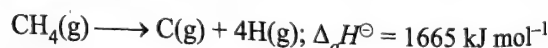
Polyatomic molecules: Let us now consider a polyatomic molecule methane, CH_4 . The overall thermochemical equation for its atomisation reaction is given below:



In methane, all the four C—H bonds are identical in bond length and energy. However, the energies required to break the individual C—H bonds in each successive step differ:



Therefore,



In such cases, we use mean bond enthalpy of C—H bond.

For example, in CH_4 , $\Delta_{\text{C-H}}H^\ominus$ is calculated as:

$$\Delta_{\text{C-H}}H^\ominus = \frac{1}{4}(\Delta_a H^\ominus) = \frac{1}{4}(1665 \text{ kJ mol}^{-1}) = 416 \text{ kJ mol}^{-1}$$

We find that mean C—H bond enthalpy in methane is 416 kJ mol^{-1} . It has been found that mean C—H bond enthalpies differ slightly from compound to compound, as in CH_4 , CH_2Cl_2 , CH_3NO_2 , etc., but it does not differ in a great deal. Using Hess' law, bond enthalpies can be calculated. Bond enthalpy values of some single and multiple bonds are given in Table 6.5.

Table 6.5 (a) Some mean single bond enthalpies in kJ mol^{-1} at 298 K

	H	C	N	O	F	Si	P	S	Cl	Br	I	
H		414	389	464	569	293	318	339	431	368	297	H
C	414		293	351	439	289	264	259	330	276	238	C
N	389	351		159	201	272	—	209	—	201	243	N
O	464	351	159		138	184	368	351	—	205	—	O
F	569	439	201	138		155	540	490	327	255	197	F
Si	293	289	272	184	155		176	213	226	360	289	Si
P	318	264	—	368	540	176		213	230	331	272	P
S	339	259	—	351	490	213	230		213	251	213	S
Cl	431	330	—	205	327	226	331	213		243	218	Cl
Br	368	276	—	—	197	289	272	218	209		192	Br
I	297	238	—	—	—	213	213	—	—	151		I

Table 6.5(b) Some mean multiple bond enthalpies in kJ mol^{-1} at 298 K

$\text{N}=\text{N}$	418	$\text{C}=\text{C}$	611	$\text{O}=\text{O}$	498
$\text{N}\equiv\text{N}$	946	$\text{C}\equiv\text{C}$	837		
$\text{C}=\text{N}$	615	$\text{C}=\text{O}$	741		
$\text{C}\equiv\text{N}$	891	$\text{C}\equiv\text{O}$	1070		

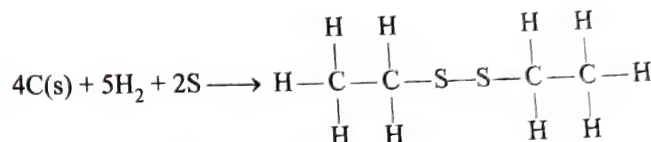
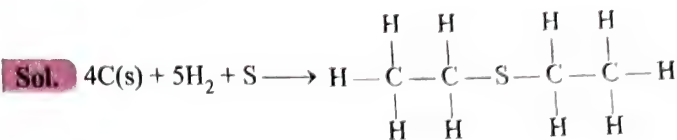
Table 6.6 Difference between bond energy and bond dissociation energy

S. No.	Bond dissociation energy	Bond energy
1.	It is the energy required to break one mole of bonds of a diatomic molecule in gaseous state e.g., $\text{H}-\text{Cl}$, $\text{H}-\text{H}$, $\text{O}=\text{O}$ etc. Since there is only one bond between two atoms (may be single bond or multiple bond), the energy required to break one mole of bonds is termed as bond dissociation energy.	Bond energy or precisely average bond energy for a polyatomic molecule is the average amount of energy required to break one mole bonds of particular type in gaseous molecules, e.g., in water molecule the bond dissociation energy of two O—H bonds differ from one another. $\text{H}-\text{O}-\text{H}(\text{g}) \rightarrow \text{OH}(\text{g}) + \text{H}(\text{g}); \Delta H = 498 \text{ kJ}$ $\text{O}-\text{H}(\text{g}) \rightarrow \text{O}(\text{g}) + \text{H}(\text{g}); \Delta H = 430 \text{ kJ}$ In such cases, the average of bond dissociation energies is termed as bond energy.
2.	It is a definite quantity and is expressed in kJ mol^{-1} .	It is an average of the various bond dissociation energies of similar bonds and is expressed in kJ mol^{-1} .

QUESTIONS BASED ON BOND ENERGY

ILLUSTRATION 6.79

Find bond enthalpy of S—S bond from the following data:



$$\Delta H = \Sigma(\text{BE})_R - \Sigma(\text{BE})_P$$

a. $-147.2 = \text{Heat of atomisation of } 4\text{C}, 10\text{H}, 1\text{S}$
 $\quad \quad \quad - \text{BE of } 10(\text{C}-\text{H}), 2(\text{C}-\text{S}), 2(\text{C}-\text{C})$

b. $-201.9 = \text{Heat of atomization of } 4\text{C}, 10\text{H}, 2\text{S}$
 $\quad \quad \quad - \text{BE of } 10(\text{C}-\text{H}), 2(\text{C}-\text{S}), 2(\text{C}-\text{C}), (\text{S}-\text{S})$

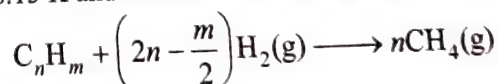
Subtracting equations (i) from (ii), we get

$$\begin{aligned} -201.9 + 147.2 &= \text{Heat of atomisation of } 1\text{S} \\ &\quad \quad \quad - \text{BE of } (\text{S}-\text{S}) \\ &= 222.8 \text{ kJ} - \text{BE of } (\text{S}-\text{S}) \end{aligned}$$

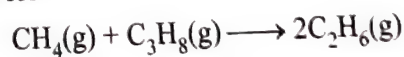
$$\text{BE of } (\text{S}-\text{S}) = 277.5 \text{ kJ}$$

ILLUSTRATION 6.80

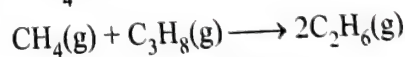
The 'heat of total cracking' of hydrocarbons ΔH_{TC} is defined as ΔH at 298.15 K and 101.325 kPa for the process below



Given that ΔH_{TC} is -65.2 kJ for C_2H_6 and -87.4 kJ for C_3H_8 , calculate ΔH for



Sol. ΔH_{TC} of $\text{CH}_4 = 0$



$$\begin{aligned} \Delta H &= 2\Delta H_{\text{TC}}(\text{C}_2\text{H}_6) - \Delta H_{\text{TC}}(\text{C}_3\text{H}_8) \\ &= 2(-65.2) - (-87.4) = -43 \text{ kJ} \end{aligned}$$

ILLUSTRATION 6.81

Bond dissociation enthalpies of $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ are $436.0 \text{ kJ mol}^{-1}$ and $941.8 \text{ kJ mol}^{-1}$, respectively, and enthalpy of formation of $\text{NH}_3(\text{g})$ is -46 kJ mol^{-1} . What is the enthalpy of atomisation of $\text{NH}_3(\text{g})$? What is the average bond enthalpy of N—H bond?

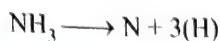
Sol. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g}); \Delta H = -2 \times 46 \text{ kJ mol}^{-1}$

$$\Delta H = \Sigma(\text{BE})_R - \Sigma(\text{BE})_P$$

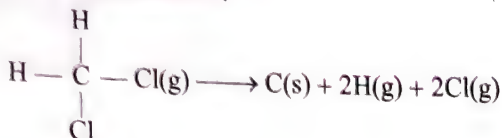
$$= (941.8 + 3 \times 436) - (6x) = -2 \times 46$$

(Here x = BE of N—H bonds)

$$x = 390.3 \text{ kJ mol}^{-1}$$



$$\text{Heat of atomisation} = 3 \times 390.3 = 1170.9 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.82Calculate ΔH of the reaction,

Bond energy for C—H bond and C—Cl bond are 400 kJ and 320 kJ, respectively.

Sol. ΔH^\ominus = Sum of bond energies of reactants
 – Sum of bond energies of products

$$= [2 \times (\text{C—H}) + 2 \times (\text{C—Cl})] - 0$$

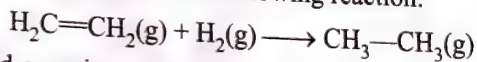
[All the products are free atoms]

$$= 2 \times 400 + 2 \times 320$$

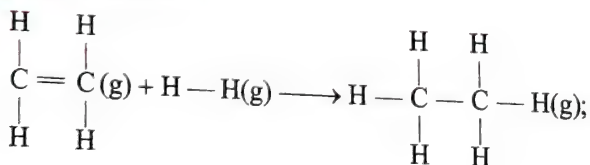
$$= 800 + 640 = 1440 \text{ kJ}$$

ILLUSTRATION 6.83

Calculate the enthalpy of the following reaction:



The bond energies of C—H, C—C, C=C, and H—H are 99, 83, 147, and 104 kcal, respectively.

Sol. The reaction is:

$$\Delta H^\ominus = \text{Sum of bond energies of reactants}$$

$$\quad \quad \quad - \text{Sum of the bond energies of products}$$

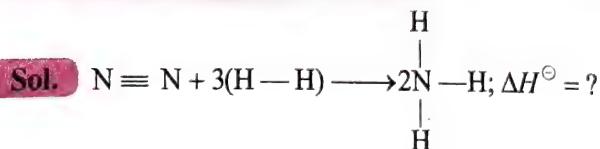
$$= [\Delta H_{\text{C}=\text{C}} + 4 \times \Delta H_{\text{C—H}} + \Delta H_{\text{H—H}}]$$

$$\quad \quad \quad - [\Delta H_{\text{C—C}} + 6 \times \Delta H_{\text{C—H}}]$$

$$= (147 + 4 \times 99 + 104) - (83 + 6 \times 99) = -30 \text{ kcal}$$

ILLUSTRATION 6.84

Calculate the enthalpy of formation of ammonia from the following bond energy data:

(N—H) bond = 389 kJ mol^{−1}; (H—H) bond = 435 kJ mol^{−1}; and (N≡N) bond = 945.36 kJ mol^{−1}.

$$\Delta H^\ominus = [\Delta H^\ominus_{(\text{N} \equiv \text{N})} + 3 \times \Delta H^\ominus_{(\text{H} - \text{H})}] - [6 \times \Delta H^\ominus_{(\text{N} - \text{H})}]$$

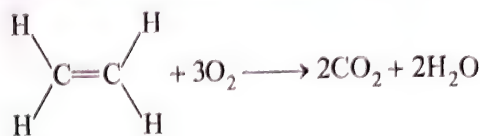
$$= 945.36 + 3 \times 435.0 - 6 \times 389.0 = -83.64 \text{ kJ}$$

$$\text{Heat of formation of NH}_3 = \frac{\Delta H^\ominus}{2} = -\frac{83.64}{2}$$

$$= -41.82 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.85

Calculate heat of combustion of ethene:



from bond energy data: C=C C—H O=O C=O O—H

BE (kJ mol^{−1}): 619 414 499 724 460

Sol. ΔH^\ominus = Sum of bond energies of reactants
 – Sum of bond energies of products

$$= [\Delta H_{(\text{C}=\text{C})} + 4\Delta H_{(\text{C—H})} + 3 \times \Delta H_{(\text{O}=\text{O})}]$$

$$\quad \quad \quad - [4 \times \Delta H_{(\text{C}=\text{O})} + 4 \times \Delta H_{(\text{O—H})}]$$

$$= [619 + 4 \times 414 + 3 \times 499] - [4 \times 724 + 4 \times 460]$$

$$= -964 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.86**I.** For the precipitation reaction of Ag⁺ ions with NaCl, which of the following statements is true?

- ΔH is zero for the reaction.
- ΔG is zero for the reaction.
- ΔG is negative for the reaction.
- ΔG should be equal to ΔH .

II. How much heat is required to change 10 g ice at 0°C to steam at 100°C? Latent heat of fusion and vaporisation for H₂O are 80 cal g^{−1} and 540 cal g^{−1}, respectively. Specific heat of water is 1 cal g^{−1}.**III.** A piston exerting a pressure of 1.0 atm rests on the surface of water at 100°C. The pressure is reduced to smaller extent and as a result 10 g of H₂O evaporates and absorbs 20 kJ of heat. Determine

- ΔH
- Latent heat of vapourisation
- W
- ΔU

Sol.**I.** c. ΔG = −ve for spontaneous process**II.** Total heat absorbed

$$= \Delta_{\text{fusion}} H + \Delta_{\text{temp. rise}} H + \Delta_{\text{vap}} H$$

$$= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200 \text{ cal}$$

III. i. ΔH = +20 kJ

ii. Moles = $\frac{10}{18} = 0.56$

⇒ Latent heat of vapourisation

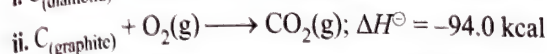
$$= \frac{\Delta H}{n} = \frac{20}{0.56} = 35.71 \text{ kJ mol}^{-1}$$

iii. $w = -nRT = -0.56 \times 8.31 \times 10^{-3} \times 373 = -1.735 \text{ kJ}$

iv. $\Delta U = \Delta H + w = 20 - 1.735 = 18.265 \text{ kJ}$

ILLUSTRATION 6.87

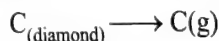
I. Determine the heat of transformation of $C_{(\text{diamond})} \longrightarrow C_{(\text{graphite})}$ from the following data:



II. Which of the following has highest heat of hydrogenation?

- a. But-1-ene b. c is-But-2-ene
c. trans-But-2-ene d. Isobutene

Sol. I. Subtracting equation (ii) from equation (i), the required equation is obtained.



$$\Delta_{\text{trans}} H^\ominus = -94.5 - (-94.0) = -94.5 + 94.0 = -0.5 \text{ kcal}$$

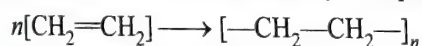
II. a. More stable is an alkene, lesser is its heat of hydrogenation

ILLUSTRATION 6.88

The bond energies of $C=C$ and $C-C$ at 298 K are 590 and 331 kJ mol^{-1} , respectively. The enthalpy of polymerisation per mole of ethylene is

- a. -70 kJ b. -72 kJ c. 72 kJ d. -68 kJ

Sol. b. The polymerisation of ethene may be represented as



one mole of $C=C$ bond is decomposed and two moles of $C-C$ bonds are formed per mole of ethene.

$$\therefore \Delta H = 590 - 2 \times 331 = -72 \text{ kJ per mol of ethylene}$$

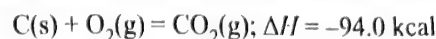
6.10.12 HESS' LAW OF CONSTANT HEAT SUMMATION

Since the molar enthalpies of reactants and products involved in a chemical reaction have definite values, it is obvious that the enthalpy change of the reaction would also have a definite value, irrespective of the way the reaction is carried out. Thus, if we transform a specified set of reactants to a specified set of products by more than one sequence of reactions, the total enthalpy change must be same for every sequence. This rule was given by the Russian chemist German Henry Hess in 1840 and is known after his name as **Hess' law**. **This rule is a consequence of the first law of thermodynamic state function and can be stated as: the heat absorbed or evolved in a given chemical reaction is the same whether the process occurs in one step or several steps.**

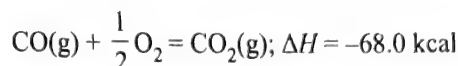
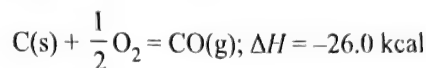
Hess' law can also be verified experimentally with the help of following examples:

a. Formation of carbon dioxide from carbon

First method: Carbon is directly converted into $CO_2(g)$.



Second method: Carbon is first converted into $CO(g)$ and then $CO(g)$ into $CO_2(g)$, i.e., conversion has been carried in two steps:



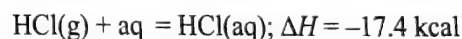
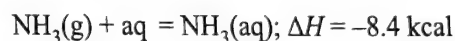
Total enthalpy change from $C(s)$ to $CO_2(g)$, $\Delta H = -94.0 \text{ kcal}$.

b. Formation of ammonium chloride from ammonia and hydrochloric acid:

First method:



Second method:



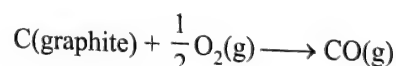
Conclusions

- The heat of formation of compounds is independent of the manner of its formation.
- The heat of reaction is independent of the time consumed in the process.
- The heat of reaction depends on the sum of enthalpies of products minus sum of the enthalpies of reactants.
- Thermochemical equations can be added, subtracted, or multiplied like algebraic equations.

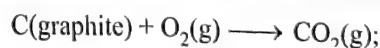
Applications of Hess' law

- For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

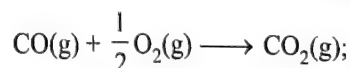
For example, ΔH for the following reaction is difficult to determine.



However, this can be determined from the following two reactions for which ΔH can be determined experimentally.

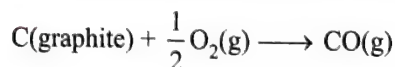


$$\Delta H_1 = -393.5 \text{ kJ mol}^{-1}$$



$$\Delta H_2 = -283.0 \text{ kJ mol}^{-1}$$

Subtracting the latter from the former, we get

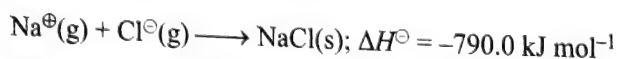


Consequently,

$$\Delta H = \Delta H_1 - \Delta H_2 = -393.3 - (-283.0) \\ = -110.5 \text{ kJ mol}^{-1}$$

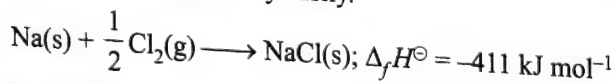
b. Lattice energy of a crystal (Born-Haber cycle)

($\Delta_{\text{lattice}}H^\ominus$): Lattice energy is defined as the amount of heat released when requisite amounts of ions in the gaseous state combine to give one mole of crystal lattice. For example, in the case of sodium chloride crystal, $\Delta_{\text{lattice}}H^\ominus$ correspond to the reaction



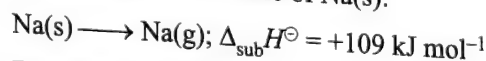
These crystal lattice energies cannot be measured directly. By applying Hess' Law to a series of elementary processes starting with $\text{Na}(\text{s})$ and $\text{Cl}_2(\text{g})$ and ending with formation of $\text{NaCl}(\text{s})$, $\Delta_{\text{lattice}}H^\ominus$ can be calculated. Such a sequence of reactions for ionic compounds is called as **Born-Haber cycle**. The concept is illustrated below by taking the formation of $\text{NaCl}(\text{s})$.

The heat of formation of sodium chloride can be calculated from bond energies very easily.

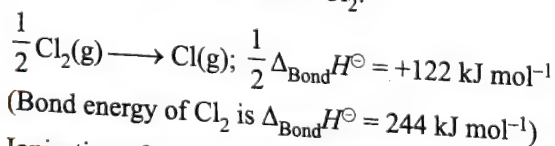


The following sequences can give the above equation:

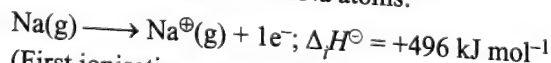
i. Sublimation of one mole of $\text{Na}(\text{s})$:



ii. Dissociation of half mole of Cl_2 :

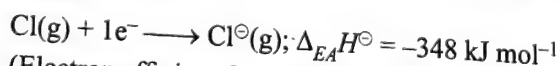


iii. Ionisation of one mole of Na atoms:



(First ionisation energy of Na atoms is 496 kJ mol^{-1})

iv. Addition of one mole of electrons to one mole of chlorine atoms:

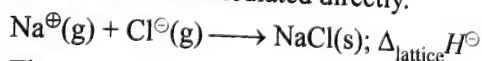


(Electron affinity of chlorine is 348 kJ mol^{-1})

(Electron affinity is the energy released, so ΔH is negative).

v. Condensation of gaseous ions to form one mole of solid NaCl :

This can not be calculated directly.



The summation of the above five reactions and their ΔH values allows us to calculate the value of $\Delta_{\text{lattice}}H^\ominus$.

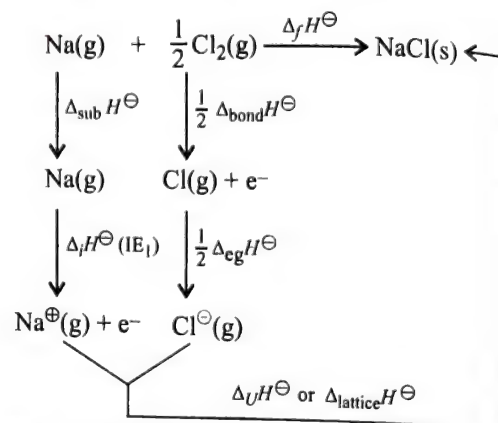
Thus, according to Hess' law;

$$\Delta_f H^\ominus = \Delta_{\text{sub}}H^\ominus + \frac{1}{2}\Delta_{\text{Bond}}H^\ominus + \Delta_i H^\ominus + \Delta_{\text{EA}}H^\ominus \\ + \Delta_{\text{lattice}}H^\ominus$$

$$-411 \text{ kJ} = 109.0 \text{ kJ} + 122.0 \text{ kJ} + 496.0 \text{ kJ} - 348.0 \text{ kJ} + \Delta_{\text{lattice}}H^\ominus$$

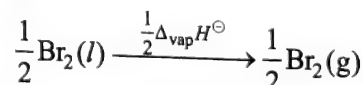
$$\therefore \Delta_{\text{lattice}}H^\ominus = -790.0 \text{ kJ mol}^{-1} \text{ of solid NaCl.}$$

Born-Haber cycle of $\text{NaCl}(\text{s})$



Born-Haber cycle of $\text{NaBr}(\text{s})$:

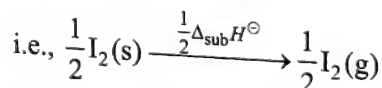
In this cycle of formation of $\text{NaBr}(\text{s})$, one more step, i.e., enthalpy of vaporisation has to be added in the Born-Haber cycle for formation of $\text{NaBr}(\text{s})$.



$$\therefore \Delta_f H^\ominus \text{ of NaBr} = \Delta_{\text{sub}}H^\ominus + \Delta_i H^\ominus + \frac{1}{2}\Delta_{\text{vap}}H^\ominus \\ + \frac{1}{2}\Delta_{\text{Bond}}H^\ominus + \frac{1}{2}\Delta_{\text{eg}}H^\ominus + \Delta_{\text{lattice}}H^\ominus$$

Born-Haber cycle of $\text{NaI}(\text{s})$

In this cycle again one more step is to be added, i.e., enthalpy of sublimation.



$$\Delta_f H^\ominus \text{ of NaI} = \Delta_{\text{sub}}H^\ominus \text{ of Na}(\text{s}) + \Delta_i H^\ominus \\ + \frac{1}{2}\Delta_{\text{sub}}H^\ominus [\text{of I}_2(\text{s})] + \frac{1}{2}\Delta_{\text{Bond}}H^\ominus \\ + \frac{1}{2}\Delta_{\text{eg}}H^\ominus + \Delta_{\text{lattice}}H^\ominus$$

c. For the determination of bond energies

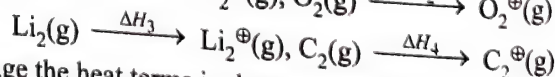
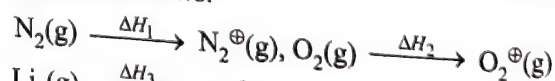
$$\Delta_f H = \Sigma \text{Bond energies of reactants}$$

$$- \Sigma \text{Bond energies of products}$$

d. For the determination of resonance energy.

ILLUSTRATION 6.89

I. The heat energy required to ionise the following molecules is given as follows:



Arrange the heat terms in decreasing order of energy:

$$\text{a. } \Delta H_1 > \Delta H_3 > \Delta H_2 > \Delta H_4$$

$$\text{b. } \Delta H_2 > \Delta H_3 > \Delta H_1 > \Delta H_4$$

$$\text{c. } \Delta H_3 > \Delta H_4 > \Delta H_1 > \Delta H_2$$

$$\text{d. } \Delta H_3 > \Delta H_1 > \Delta H_4 > \Delta H_2$$

- II. The enthalpy of a reaction does not depend upon:
- the intermediate reaction steps
 - the temperature of initial and final state of the reaction
 - the physical states of reactants and products
 - use of different reactants for the formation of the same product

Sol. I. b. Enthalpy of ionisation depends upon the size of molecules. Larger the size lesser will be ionisation energy.

II. d. (According to Hess' law)

ILLUSTRATION 6.90

I. The heat change at constant volume for the decomposition of silver(I) oxide is found to be 30.66 kJ. The heat change at constant pressure will be

- 30.66 kJ
- >30.66 kJ
- <30.66 kJ
- Unpredictable

II. i. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}); \Delta H = -x \text{ kJ}$

ii. $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}; \Delta H = -y \text{ kJ}$

iii. $2\text{H}_2\text{O} + 2\text{Cl}_2 \longrightarrow 4\text{HCl} + \text{O}_2; \Delta H = -z \text{ kJ}$

From the above equations, the value of $\Delta_f H$ of HCl is

- $-x \text{ kJ}$
- $-y \text{ kJ}$
- $-z \text{ kJ}$
- $-\frac{x}{2} \text{ kJ}$

III. $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + X \text{ kJ}$

$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + Y \text{ kJ}$

The enthalpy of formation of NO is

- $(2X - 2Y)$
- $X - Y$
- $1/2(Y - X)$
- $1/2(X - Y)$

Sol.

I. b. $\text{Ag}_2\text{O}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g});$

$$(\Delta U)_V = 30.66 \text{ kJ}$$

We know that

$$\Delta H = \Delta U + \Delta nRT;$$

$$= 30.66 + \frac{3}{2} \times R \times T$$

$$\left(\begin{array}{l} \Delta n = n_p - n_R \\ = \frac{5}{2} - 1 = \frac{3}{2} \end{array} \right)$$

$$\therefore \Delta H > \Delta U$$

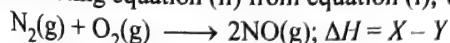
II. d. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}); \Delta H = -x \text{ kJ}$

$$\therefore \text{For 1 mole of HCl, } \Delta H = \frac{-x}{2} \text{ kJ mol}^{-1}$$

III. d. $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}); \Delta H = +X \text{ kJ} \quad \dots(i)$

$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}); \Delta H = +Y \text{ kJ} \quad \dots(ii)$

Subtracting equation (ii) from equation (i), we get



$$\text{or } \Delta_f H^\ominus(\text{NO}) = \frac{(X - Y)}{2} \text{ kJ mol}^{-1}$$

QUESTIONS BASED ON LATTICE HYDRATION ENERGY AND BORN-HABER CYCLE

ILLUSTRATION 6.91

The lattice energy of solid NaCl is $180 \text{ kcal mol}^{-1}$. The dissolution of the solid in H_2O is endothermic to the extent of $1.0 \text{ kcal mol}^{-1}$. If the hydration energies of Na^\oplus and Cl^\ominus ions are in the ratio of 6:5 what is the enthalpy of hydration of sodium ion?

- $-85 \text{ kcal mol}^{-1}$
- $-98 \text{ kcal mol}^{-1}$
- $+82 \text{ kcal mol}^{-1}$
- $+100 \text{ kcal mol}^{-1}$

Sol. b. We know that

Enthalpy of solution = Lattice energy + Hydration enthalpy

$$\text{or } \Delta_{\text{sol}} H^\ominus = \Delta_{\text{lattice}} H^\ominus + \Delta_{\text{hyd}} H^\ominus$$

$$\therefore \Delta_{\text{hyd}} H^\ominus = \Delta_{\text{sol}} H^\ominus - \Delta_{\text{lattice}} H^\ominus = 1.0 - 180$$

$$= -179.0 \text{ kcal mol}^{-1}$$

The ratio of hydration energies of Na^\oplus and Cl^\ominus is 6:5.

$$\therefore \text{Hydration energy of } \text{Na}^\oplus = \frac{6}{11} \times (-179.0)$$

$$= -97.63 \text{ kcal} \approx -98.0 \text{ kcal}$$

ILLUSTRATION 6.92

Given:

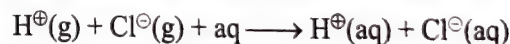
i. $\text{H}(\text{g}) + \text{Cl}(\text{g}) \longrightarrow \text{HCl}(\text{g}) \quad \Delta H_1 = -431 \text{ kJ}$

ii. $\text{HCl}(\text{g}) + \text{aq} \longrightarrow \text{H}^\oplus(\text{aq}) + \text{Cl}^\ominus(\text{aq}) \quad \Delta H_2 = -75.1 \text{ kJ}$

iii. $\text{H}(\text{g}) \longrightarrow \text{H}^\oplus(\text{g}) + \text{e}^- \quad \Delta H_3 = 1317 \text{ kJ}$

iv. $\text{Cl}(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^\ominus(\text{g}) \quad \Delta H_4 = -354 \text{ kJ}$

a. Calculate the enthalpy of hydration of HCl



b. Calculate the enthalpy of hydration of Cl^\ominus ions if enthalpy of hydration of H^\oplus is zero.

Sol.

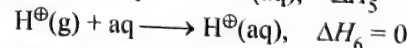
a. $\text{H}^\oplus(\text{g}) + \text{Cl}^\ominus(\text{g}) + \text{aq} \longrightarrow \text{H}^\oplus(\text{aq}) + \text{Cl}^\ominus(\text{aq}) \quad \Delta H = ?$

$$\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4$$

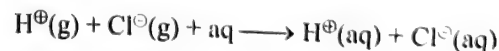
$$= -431 - 75.1 - 1317 - (-354)$$

$$= -1469.1 \text{ kJ}$$

b. $\text{Cl}^\ominus(\text{g}) + \text{aq} \longrightarrow \text{Cl}^\ominus(\text{aq}), \quad \Delta H_5 = ?$



Given:



$$\Delta H = -1469.1 \text{ kJ}$$

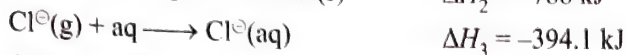
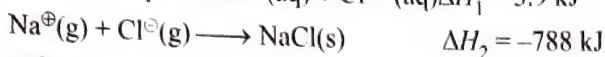
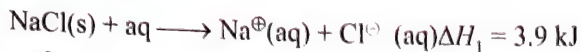
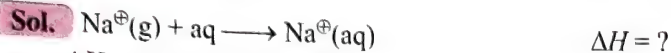
$$\Delta H = \Delta H_5 + \Delta H_6$$

$$\therefore \Delta H_5 = \Delta H - \Delta H_6$$

$$= -1469.1 - 0 = -1469.1 \text{ kJ}$$

ILLUSTRATION 6.93

Given:

Calculate the enthalpy of hydration of Na^{\oplus} ions $\Delta h = ?$.

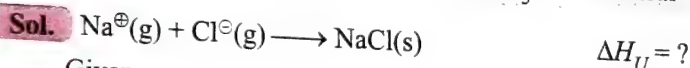
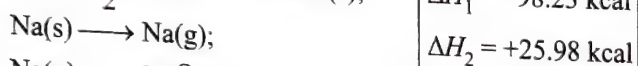
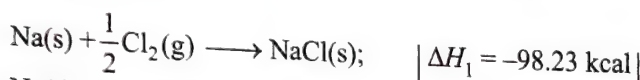
$$\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3$$

$$= 3.9 - 788 - (-394.1)$$

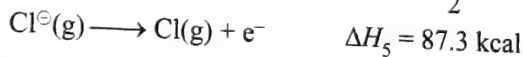
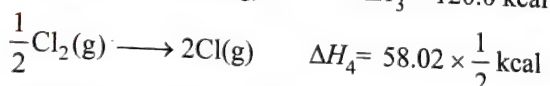
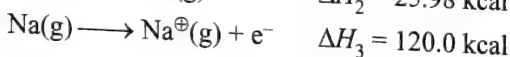
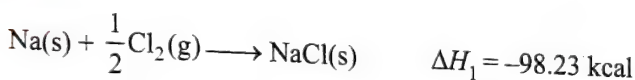
$$= 3.9 - 788 + 394.1 = -390.0 \text{ kJ}$$

ILLUSTRATION 6.94

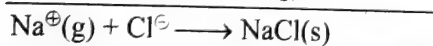
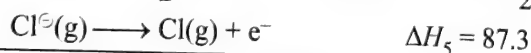
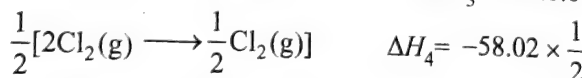
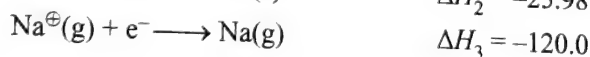
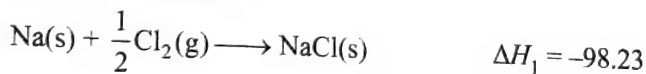
How much heat is liberated when one mole of gaseous Na^{\oplus} combines with one mole of Cl^{\ominus} ion to form solid NaCl . Use the data given below:



Given:



Rewriting equations:



$$\Delta H = 98.23 - 25.98 - 120.0 - 58.02 \times \frac{1}{2} + 87.3$$

$$= -185.92 \text{ kcal}$$

or

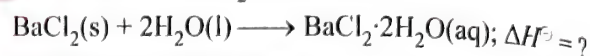
$$\Delta H = \Delta H_1 - \Delta H_2 - \Delta H_3 - \frac{1}{2}\Delta H_4 + \Delta H_5$$

$$= -98.23 - 25.98 - 120.0 - \frac{1}{2} \times 58.02 + 87.3$$

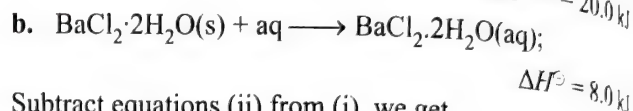
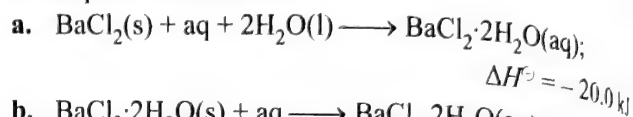
$$= -185.92 \text{ kcal}$$

ILLUSTRATION 6.95

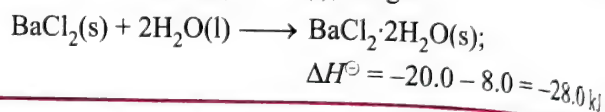
Enthalpies of solution of $\text{BaCl}_2(\text{s})$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ are $-20.0 \text{ kJ mol}^{-1}$ and 8.0 kJ mol^{-1} , respectively. Calculate $\Delta_{\text{hyd}} H^\ominus$ of BaCl_2 to $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

Sol. Hydration of BaCl_2 is given as

Enthalpies of solution are



Subtract equations (ii) from (i), we get



Applications of Bond Enthalpy

a. Determination of enthalpy of reaction: The reaction enthalpy are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of the new bonds. We can predict enthalpy of a reaction in gas phase, if we know different bond enthalpies. The standard enthalpy of reaction, $\Delta_r H^\ominus$ is related to bond enthalpies of the reactants and $\Delta_r H^\ominus$ products in gas phase reactions as:

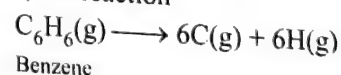
$$\Delta_r H^\ominus = \sum \text{Bond enthalpies}_{\text{reactants}} - \sum \text{Bond enthalpies}_{\text{products}}$$

This relationship is particularly more useful when the required values of $\Delta_r H^\ominus$ are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Remember that this relationship is approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

b. Determination of resonance energy: When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

$$\text{Resonance energy} = \text{Experimental heat of formation} - \text{Calculated heat of formation}$$

For example, the reaction



will require enthalpy of 5368.5 kJ. On the basis of bond enthalpies ($3\text{H}_{\text{C-C}} + 3\text{H}_{\text{C=C}} + 6\text{H}_{\text{C-H}} = 3 \times 347.69 \text{ kJ} + 3 \times 615.05 \text{ kJ} + 6 \times 413.38 \text{ kJ} = 5368.5 \text{ kJ mol}^{-1}$), where the experimental value is $5535.1 \text{ kJ mol}^{-1}$. Thus, the resonance energy is $= (5535.1 - 5368.5) \text{ kJ mol}^{-1} = 166.6 \text{ kJ mol}^{-1}$. This amounts to the fact that benzene is more stable by $166.6 \text{ kJ mol}^{-1}$. This is due to resonance, that is, in benzene there is no localization of single and double bonds, but the molecule is resonating from one extreme to another.

Notes:

- For any elementary substance appearing in the reaction, the heat of formation under standard state is taken as zero.
- In case of allotropes, the enthalpy of formation of the most stable allotrope is taken as zero, e.g., the heat of formation of graphite is zero but of diamond is not zero. Similarly, standard enthalpy of rhombic sulphur is zero.
- Heat of combustion is always negative.
- a. Calorific value is the amount of heat evolved when one gram of fuel or food is burnt in the presence of air or excess of oxygen.
b. Heat of combustion is used to calculate calorific value of fuels i.e., heat of combustion per gm or per mL. Greater the value more effective is the fuel.
- An adult requires 2500 to 3000 kcal of energy per day.
- During dissolution, physical state of the compound changes while during hydration, there is no change in the physical state of the compound.
- Heat of solution can be +ve as well as -ve.
- Enthalpy of neutralization of a strong acid and strong base is always -57.1 kJ or -13.7 Kcal.
- Trouton's rule. The ratio of enthalpy of vaporisation and the normal boiling point of a liquid approximately equals $88 \text{ J/mol}^{-1} \text{ K}^{-1}$

i.e. $\frac{\Delta H_{\text{vap}}}{T_b} \approx 88 \text{ J mol}^{-1} \text{ K}^{-1}$

- Heat of combustion of organic substances and heat of hydrogenation are determined in Bomb calorimeter.
- Heat of neutralization is determined by using calorimeter or Dewar flask.
- For expansion of ideal gas in vacuum adiabatically, no cooling occurs.
- The value of inversion temperature can be calculated using van der Waals' equation $T_i = \frac{2a}{R \times b}$ (where a and b are van der Waals' constant of the gas)
- If the solubility of a substance is known at two different temperatures, the mean molar enthalpy of solution over this temperature range can be calculated by applying an equation similar to van't Hoff equation (relating equilibrium equation with temperature).

$$\therefore \log \frac{S_1}{S_2} = \frac{\Delta H}{2.303T} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

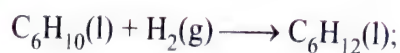
where S_1 and S_2 are solubilities at temperatures T_1 and T_2 , respectively.

QUESTIONS BASED ON RESONANCE ENERGY

ILLUSTRATION 6.96

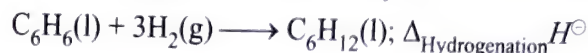
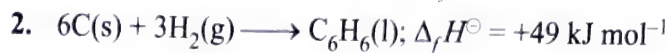
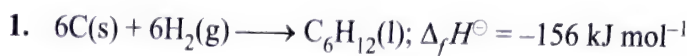
The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are -156 and $+49 \text{ kJ mol}^{-1}$, respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is -119 kJ mol^{-1} . Use this data to estimate the magnitude of the resonance energy of benzene.

Sol. Given:



$$\Delta_{\text{Hydrogenation}} H^\ominus = -119 \text{ kJ mol}^{-1}$$

Find the actual heat of hydrogenation of benzene from Hess's law as follows:



$$\Rightarrow (\Delta_{\text{Hydrogenation}} H^\ominus)_{\text{Actual}} = -156 - 49 = -205 \text{ kJ mol}^{-1}$$

Note: $\Delta_{\text{Hydrogenation}} H^\ominus$ is always negative.

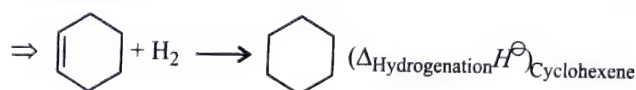
Now,

$$\left(\begin{array}{c} \text{Hypothetical heat of} \\ \text{hydrogenation of benzene} \end{array} \right) \equiv \left(\begin{array}{c} \text{Heat of hydrogenation} \\ \text{of cyclo hexatriene} \end{array} \right)$$

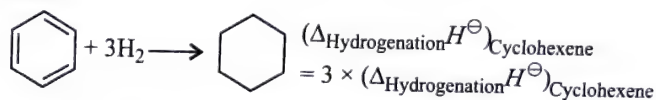
$$\equiv 3 \times \left(\begin{array}{c} \text{Heat of hydrogenation} \\ \text{of cyclohexane} \end{array} \right)$$

$$= 3 \times (-119) = -357 \text{ kJ mol}^{-1}$$

Here, we have assumed that there are only 3 double bonds in benzene (Kekule's structure) and in hydrogenating it, the energy obtained will be roughly 3 times of hydrogenating cyclohexene.



and

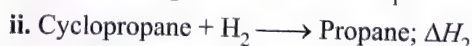


Clearly, heat of hydrogenation for theoretical benzene is more negative and thus, it is less stable. So, resonance energy should be negative (since actual benzene is more stable).

$$\Rightarrow \text{Resonance energy} = -357 - (-205) = -152 \text{ kJ mol}^{-1} \text{ of benzene}$$

ILLUSTRATION 6.97

Consider the following two reactions:



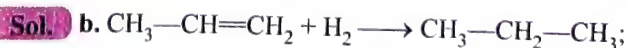
Then, $\Delta H_2 - \Delta H_1$ will be:

a. 0

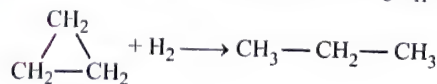
b. $2\text{BE}_{\text{C}-\text{C}} - \text{BE}_{\text{C}=\text{C}}$

c. $\text{BE}_{\text{C}=\text{C}}$

d. $2\text{BE}_{\text{C}=\text{C}} - \text{BE}_{\text{C}-\text{C}}$



$$\Delta H_1 = (\text{BE}_{\text{C}=\text{C}} + \text{BE}_{\text{H}-\text{H}}) - (2\text{BE}_{\text{C}-\text{H}} + \text{BE}_{\text{C}-\text{C}})$$



$$\Delta H_2 = (\text{BE}_{\text{C}-\text{C}} + \text{BE}_{\text{H}-\text{H}}) - (2 \times \text{BE}_{\text{C}-\text{H}})$$

$$\Delta H_2 - \Delta H_1 = 2\text{BE}_{\text{C}-\text{C}} - \text{BE}_{\text{C}=\text{C}}$$

ILLUSTRATION 6.98

Calculate the resonance energy of gaseous benzene from the following data.

$$\text{BE}(\text{C—H}) = 416.3 \text{ kJ mol}^{-1}$$

$$\text{BE}(\text{C—C}) = 331.4 \text{ kJ mol}^{-1}$$

$$\text{BE}(\text{C}=\text{C}) = 591.1 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{sub}} H^\ominus(\text{C, graphite}) = 718.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{diss}} H^\ominus(\text{H}_2, \text{g}) = 435.9 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus(\text{benzene, g}) = 82.9 \text{ kJ mol}^{-1}$$

Sol. To compute resonance energy, we compare the calculated value of $\Delta_f H^\ominus(\text{benzene, g})$ with the given one. To calculate $\Delta_f H^\ominus(\text{benzene, g})$, we add the following reactions.



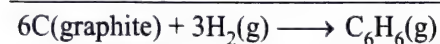
$$\Delta H^\ominus = -(3\text{BE}_{\text{C—C}} + 3\text{BE}_{\text{C}=\text{C}} + 6\text{BE}_{\text{C—H}})$$



$$\Delta H^\ominus = 6 \times 718.4 \text{ kJ mol}^{-1}$$



$$\text{Add (a + b + c)} \quad \Delta H^\ominus = 3 \times 435.9 \text{ kJ mol}^{-1}$$



The corresponding enthalpy change is

$$\begin{aligned} \Delta_f H^\ominus &= -(3\text{BE}_{\text{C—C}} + 3\text{BE}_{\text{C}=\text{C}} + 6\text{BE}_{\text{C—H}}) \\ &\quad + [6 \times 718.4 + 3 \times 435.9] \text{ kJ mol}^{-1} \\ &= [-(3 \times 331.4 + 3 \times 591.1 + 6 \times 416.3 + 3 \\ &\quad \times 435.9) \text{ kJ mol}^{-1} \end{aligned}$$

The given $\Delta_f H^\ominus$ is $\Delta_f H^\ominus(\text{benzene, g}) = 82.9 \text{ kJ mol}^{-1}$

This means benzene becomes more stable by $(352.8 - 82.9) \text{ kJ mol}^{-1}$, i.e., $269.7 \text{ kJ mol}^{-1}$.

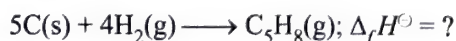
This is its resonance energy.

ILLUSTRATION 6.99

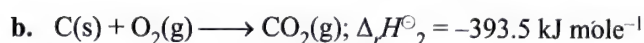
Calculate the resonance energy of isoprene (C_5H_8) from the data given.

Standard Heats of combustion of isoprene, carbon, and hydrogen are -3186 , -393.5 , and $-285.83 \text{ kJ mol}^{-1}$, respectively. Bond energies of $\text{C}=\text{C}$, C—C , C—H , and H—H bonds are 615 , 348 , 413 , and $435.8 \text{ kJ mol}^{-1}$ respectively. Standard heat of sublimation of graphite is $718.3 \text{ kJ mol}^{-1}$.

Sol. Calculate $\Delta_f H^\ominus$ of isoprene from its heat of combustion (This will give the value for actual isoprene existing in nature).



$$\Delta_f H^\ominus_1 = -3186 \text{ kJ mole}^{-1}$$



$$\Delta_f H^\ominus_3 = -285.83 \text{ kJ mole}^{-1}$$

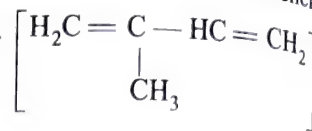
Now operating $5(b) + 4(c) - (a)$ to get the equation of formation.

$$\Delta_f H^\ominus = 5\Delta_f H^\ominus_b + 4\Delta_f H^\ominus_c - \Delta_f H^\ominus_a$$

$$\Rightarrow \Delta_f H^\ominus = 5(-393.5) + 4(-285.83) - (-3186)$$

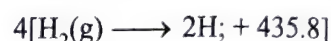
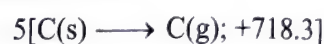
$$\Rightarrow (\Delta_f H^\ominus)_{\text{actual}} = 75.18 \text{ kJ mol}^{-1}$$

Now calculate the heat of formation using the bond energy and structure of isoprene.



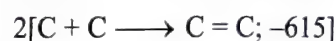
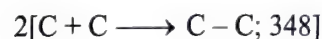
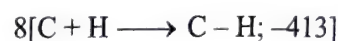
Note:

i. Bond breaking: (ΔH_1)



$$\Rightarrow \Delta H_1 = 5 \times 718.3 + 4 \times 435.8 = +5334.7 \text{ kJ}$$

ii. Bond formation: (ΔH_2)



$$\Rightarrow \Delta H_2 = -(8 \times 413 + 2 \times 348 + 2 \times 615) = -5230 \text{ kJ}$$

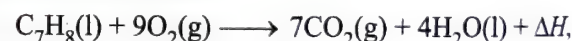
From Hess' Law : ($\Delta_f H^\ominus$)_{Theoretical} = $\Delta H_1 + \Delta H_2$

$$(\Delta_f H^\ominus)_{\text{Theoretical}} = 5334.7 + (-5230) = 104.7 \text{ kJ}$$

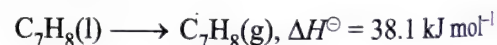
$$\Rightarrow \text{Resonance energy} = 75.18 - 104.7 = -29.52 \text{ kJ}$$

ILLUSTRATION 6.100

Calculate the resonance energy of toluene (use Kekule structure) from the following data



$$\Delta H^\ominus = -3910 \text{ kJ mol}^{-1}$$



$$\Delta_f H^\ominus(\text{water}) = -285.8 \text{ kJ mol}^{-1}$$

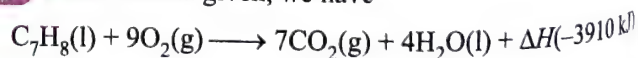
$$\Delta_f H^\ominus[\text{CO}_2(\text{g})] = -393.5 \text{ kJ mol}^{-1}$$

$$\text{Heat of atomisation of H}_2(\text{g}) = 436.0 \text{ kJ mol}^{-1}$$

$$\text{Heat of sublimation of C(g)} = 715.0 \text{ kJ mol}^{-1}$$

Bond energies of C—H , C—C , and $\text{C}=\text{C}$ are 413.0 , 345.6 , and $610.0 \text{ kJ mol}^{-1}$.

Sol. From the data given, we have



It is known that

$$\Delta H^\ominus(\text{reaction}) = (\Sigma_f H^\ominus)(\text{products}) - (\Sigma_f H^\ominus)(\text{reactants})$$

$$= (4 \times \Delta_f H^\ominus_{\text{H}_2\text{O}}(\text{l}) + 7 \times \Delta_f H^\ominus_{\text{CO}_2}) - \Delta_f H^\ominus[\text{C}_7\text{H}_8(\text{l})]$$

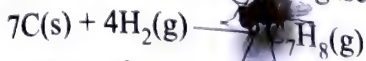
$$\text{or } -3910 = [4 \times (-285) + 7(-393.5)] - \Delta_f H^\ominus[\text{C}_7\text{H}_8(\text{l})]$$

$$\text{or } \Delta_f H^\ominus \text{C}_7\text{H}_8(\text{l}) = (3910 - 2754.5 - 1143.2) \text{ kJ}$$

$$= 12.3 \text{ kJ mol}^{-1}$$

$$\therefore \Delta_f H^\ominus \text{ for gaseous toluene} = (12.3 + 38.1) \text{ kJ} = 50.4 \text{ kJ}$$

Chemical equation for the formation of gaseous toluene



$$(\Delta_f H^\ominus)_{\text{cal}} = [7 \times (\text{heat of sublimation of solid C}$$

$$+ 4\text{BE of H}_2\text{(g)})$$

$$= -3 \times \text{C}=\text{C} + 4 \times \text{C}-\text{C} + 8 \times \text{C}-\text{H}]$$

$$= (7 \times 715 + 4 \times 436) - (3 \times 610 + 4 \times 345.6 + 8 \times 413)$$

$$= (5005 + 1744) - (1830 + 3304 + 1382.4)$$

$$= (6749.0 - 6516.4) \text{ kJ} = 232.6 \text{ kJ}$$

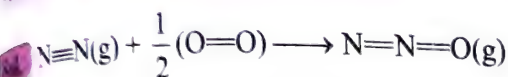
$$\text{Resonance energy} = (232.6 - 50.40) \text{ kJ} = 182.2 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.101

Calculate the resonance energy of N_2O from the following data

$$\Delta_f H^\ominus \text{ of } \text{N}_2\text{O} = 82 \text{ kJ mol}^{-1}$$

Bond energy of $\text{N}\equiv\text{N}$, $\text{N}=\text{N}$, $\text{O}=\text{O}$, and $\text{N}=\text{O}$ bonds is 946, 418, 498, and 607 kJ mol^{-1} , respectively.



$$\Delta_f H^\ominus (\text{N}_2\text{O}) = [\Delta H^\ominus (\text{N}\equiv\text{N}) + \frac{1}{2} \Delta H^\ominus (\text{O}=\text{O})] - [\Delta H^\ominus (\text{N}=\text{O}) + \Delta H^\ominus (\text{N}=\text{N})]$$

$$= \left(946 + \frac{1}{2} \times 498 \right) - (607 + 418)$$

$$= 946 + 249 - 607 - 418$$

$$= 1195 - 1025 = 170 \text{ kJ mol}^{-1}$$

Resonance energy = Observed heat of formation

– Calculated heat of formation

$$= 82 - 170 = -88 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.102

Enthalpy of hydrogenation of benzene is ΔH_1 and for cyclohexene is ΔH_2 . The resonance energy of benzene is

a. $3\Delta H_1 - \Delta H_2$

b. $3\Delta H_2 - \Delta H_1$

c. $3\Delta H_1 + \Delta H_2$

d. $\Delta H_1 - 3\Delta H_2$

b. Heat of hydrogenation is always negative and benzene is more stable than cyclohexatriene.

Therefore, resonance energy should be negative.

$$\therefore 3\Delta H_2 - \Delta H_1$$

CONCEPT APPLICATION EXERCISE 6.3

Subjective Type

- Find the heat that of sublimation of sodium metal from the following data. Ionisation energy of sodium = 502.1, bond energy of chlorine = 242.8, heat of formation of $\text{NaCl} = -411.1$, lattice energy of $\text{NaCl} = -778.0$, and electron affinity of chlorine is -365.3 . All units are in kJ mol^{-1} .
- An athlete takes 20 breaths per minute at room temperature. The air inhaled in each breath is 200 mL which contains

20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all oxygen is consumed if used for converting glucose into CO_2 and $\text{H}_2\text{O(l)}$, how much glucose will be burnt in the body in one hour and what is the heat produced. (Room temperature = 27°C and enthalpy of combustion of glucose is $-2822.5 \text{ kJ mol}^{-1}$ at 0°C).

- Calculate the resonance energy of C_6H_6 using kekule formula of C_6H_6 from the following data.

a. $\Delta_f H^\ominus$ for $\text{C}_6\text{H}_6 = -358.5 \text{ kJ mol}^{-1}$

b. Heat of atomisation of $\text{C} = 716.8 \text{ kJ mol}^{-1}$

c. Bond energy of $\text{C}-\text{H}$, $\text{C}-\text{C}$, $\text{C}=\text{C}$ and $\text{H}-\text{H}$ are 490, 620, 436.9 kJ mole^{-1} respectively.

- A person inhales 640 g of O_2 per day. If all the O_2 is used for converting sugar into CO_2 and H_2O , how much sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is consumed in the body in one day and what is the heat evolved.

$$(\Delta H_{\text{Combustion of sucrose}} = -5645 \text{ kJ mol}^{-1})$$

- ΔH combustion for CH_4 , C_2H_6 , and C_3H_8 are -210.8 , -368.4 and $-526.3 \text{ kcal mol}^{-1}$, respectively. Calculate ΔH combustion for octane.

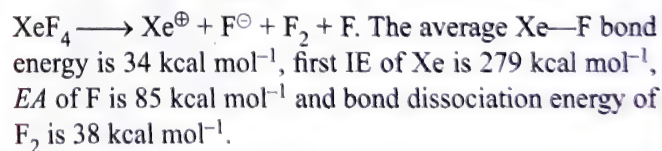
- When 12.0 g of C reacted with a limited quantity of oxygen, 57.5 kcal of heat was produced. Calculate the number of CO and number of moles of CO_2 produced.

$$\text{Given } \text{C} + \text{O}_2 \longrightarrow \text{CO}_2; \Delta_f H = -94.05 \text{ kcal}$$

$$\text{C} + 1/2\text{O}_2 \longrightarrow \text{CO}; \Delta_f H = -26.41 \text{ kcal}$$

- Given $\text{CaCl}_2\text{(s)} + \text{aq} \longrightarrow \text{CaCl}_2\text{(aq)} : \Delta H^\ominus = 75 \text{ kJ mol}^{-1}$ at 18°C and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{aq} \longrightarrow \text{CaCl}_2\text{(aq)}, \Delta H^\ominus = 19 \text{ kJ mol}^{-1}$ at 18°C . Find the heat of hydration of CaCl_2 to $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ by $\text{H}_2\text{O(g)}$. The Heat of vaporisation of water may be taken as $2452 \text{ J}^{-1} \text{ g}$ at 18°C .

- Calculate the enthalpy change for the following reaction:



- The conversion of gaseous atoms K and F to ions K^\oplus and F^\ominus absorbs 0.85 eV . If the ionization energy and electron affinity of K and F have magnitudes in the ratio $7 : 6$, what is the electron affinity of fluorine?

- Calculate the enthalpy change when infinitely dilute solution of CaCl_2 and Na_2CO_3 are mixed. $\Delta_f H^\ominus$ for $\text{Ca}^{2+}(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$, and $\text{CaCO}_3\text{(s)}$ are -129.80 , -161.65 , and $-288.50 \text{ kcal mol}^{-1}$ respectively.

- The sublimation energy of a metal is 100 kJ mol^{-1} and its 1st and 2nd IEs are 4.0 eV and 12.0 eV respectively. The hydration energy of X^\oplus is -380 kJ mol^{-1} and X^{2+} is $-1280 \text{ kJ mol}^{-1}$. Comment the stability of two ions in water.

- The $\text{C}-\text{H}$ bond of the side chain in toluene, $\text{C}_6\text{H}_5-\text{CH}_3$, has a dissociation energy of $77.5 \text{ kcal mol}^{-1}$. Calculate

$\Delta_f H^\ominus$ of benzyl radical and the strength of the central bond in dibenzyl $\text{C}_6\text{H}_5\text{—CH}_2\text{—CH}_2\text{—C}_6\text{H}_5$ given that $\Delta_f H^\ominus$ to toluene vapour is 12 kcal mol^{-1} and that of dibenzyl vapour is $27.8 \text{ kcal mol}^{-1}$. BE of $\text{H}_2 = 104 \text{ kcal mol}^{-1}$.

13. a. Cis-2-butene \longrightarrow trans-2-butane, ΔH_1
 b. Cis-2-butene \longrightarrow 1-butene, ΔH_2
 c. Trans-2-butene is more stable than Cis-2-butene
 d. Enthalpy of combustion of 1-butene,
 $\Delta H = -649.8 \text{ kcal/mol}$
 e. $9\Delta H_1 + 5\Delta H_2 = 0$
 f. Enthalpy of combustion of trans-2-butene,
 $\Delta H = -647.1 \text{ kcal mol}^{-1}$.
 Calculate ΔH_1 and ΔH_2 ?

14. Calculate the proton affinity of $\text{NH}_3(\text{g})$ from the following data (in kJ mol^{-1}):

$\Delta_f H^\ominus$ dissociation: $\text{H}_2(\text{g}) = 218$

$\Delta_f H^\ominus$ formation: $\text{NH}_3(\text{g}) = -46$

Lattice energy of $\text{NH}_4\text{Cl}(\text{s}) = 683$

Ionisation energy of $\text{H} = 1310$

Electron affinity of $\text{Cl} = -348$

Bond dissociation energy $\text{Cl}_2(\text{g}) = 124$

$\Delta_f H^\ominus(\text{NH}_4\text{Cl}) = -314$

15. Calculate the enthalpy of combustion of benzene (l) on the basis of the following data:

a. Resonance energy of benzene (l) = -152 kJ/mol

b. Enthalpy of hydrogenation of cyclohexene (l) = -119 kJ/mol

c. $\Delta_f H^\ominus \text{C}_6\text{H}_{12}(\text{l}) = -156 \text{ kJ mol}^{-1}$

d. $\Delta_f H^\ominus$ of $\text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ mol}^{-1}$

e. $\Delta_f H^\ominus$ of $\text{CO}_2(\text{g}) = -393.5 \text{ kJ mol}^{-1}$

16. Find ΔH of the process:



Given:

$\Delta_{\text{diss}} H^\ominus$ of $\text{O}_2 = 151 \text{ kJ mol}^{-1}$

$\Delta_{\text{diss}} H^\ominus$ of $\text{H}_2 = 435 \text{ kJ mol}^{-1}$

$\Delta_{\text{diss}} H^\ominus$ of $\text{O—H} = 465 \text{ kJ mol}^{-1}$

$\Delta_{\text{diss}} H^\ominus$ of $\text{Na—O} = 255 \text{ kJ mol}^{-1}$

$\Delta_{\text{soln}} H^\ominus$ of $\text{NaOH} = -46 \text{ kJ mol}^{-1}$

$\Delta_f H^\ominus$ of $\text{NaOH}(\text{s}) = -427 \text{ kJ mol}^{-1}$

$\Delta_{\text{sub}} H^\ominus$ of $\text{Na}(\text{s}) = 109 \text{ kJ mol}^{-1}$

ANSWERS

Subjective Type

1. $108.7 \text{ kJ mol}^{-1}$
2. 458.66 kJ
3. $150.0 \text{ kJ mol}^{-1}$
4. 9408.34 kJ
5. -1315.5 kcal

6. $0.46 \text{ mol of CO}_2, 0.54 \text{ mol CO}$

7. $-358.816 \text{ kJ mol}^{-1}$

9. 5.10 eV

10. 2.95 kcal

11. $\text{X}^{2+}(\text{aq})$ more stable than X^\oplus

12. $47.2 \text{ kcal mol}^{-1}$

13. $\Delta H_1 = -0.96 \text{ kcal}; \Delta H_2 = 1.74 \text{ kcal}$

14. -718 kJ mol^{-1}

15. $-3267.4 \text{ kJ mol}^{-1}$

8. 292 kJ mol^{-1}

16. $+159 \text{ kJ mol}^{-1}$

6.11 LIMITATIONS OF THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is concerned with the conversion of energy from one form to another. It helps us to understand energy transformation in different chemical reactions. The basic point of first law is that all physical and chemical processes take place in such a manner that the total energy of the universe (i.e., the energy of the system and the energy of the surroundings) is constant. However, it suffers from the following limitations:

- a. The first law is unable to predict the direction of change or feasibility of the process in particular direction. It is clear from the following examples:

A hot object cools down to the temperature of the surroundings but an object does not become hotter than its surroundings of its own. For example, when a cup of hot tea is kept in a room, it cools spontaneously by losing heat to the surroundings. Obviously, the first law of thermodynamics is obeyed because the energy lost by the system (i.e., the cup of tea) is gained by the surroundings. However, we never observe an amusing situation where a cup of tea at room temperature becomes hot of its own. The first law will still be obeyed in this reverse process when the surroundings lose energy and the system gains it. But it never happens. In other words, the cooling of a hot body in a room proceeds spontaneously but not its heating, though both the processes are in accordance with the first law of thermodynamics.

A gas expands to fill the space available to it. However, it does not contract to a smaller volume of its own.

If we add a drop of ink in a beaker containing water, the ink spreads spontaneously throughout the beaker making the whole solution coloured. But we have never seen the reverse process where the dispersed ink spontaneously accumulates to form a drop of ink.

- b. The first law of thermodynamics does not give any information about the extent to which the change takes place. For example, it is practically found that whole of heat can never be converted into work. Thus, first law fails to tell the extent to which the interchange of heat into work and vice-versa is possible.

The above examples show the insufficiency of first law of thermodynamics. The first law does not determine the feasibility or spontaneity of a process. The spontaneity or feasibility of a

physical or a chemical process is decided by the second law of thermodynamics. Let us first understand what do we mean by spontaneous reaction or change.

6.12 SPONTANEOUS PROCESS OR SPONTANEITY

In our daily life, we come across many natural processes which occur on their own in one direction only. For example, water flows down the hill without the help of external agency but water cannot flow up the hill on its own. Similarly, a glass of hot water placed in the room gradually cools and attains room temperature. The glass of water cannot become hot on its own. It can, however, be made hot by the use of external agency, i.e., some heating device.

Such processes are called spontaneous processes.

Thus, the spontaneous process may be defined as an irreversible process. A process that can take place by itself under the given set of conditions once it has been initiated, if necessary, is said to be a *spontaneous process*. In other words, a spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called *feasible* or *probable* processes. It may be noted that the term spontaneous should not be taken to mean that the process occurs instantaneously. It simply predicts that the process has natural tendency to occur. The actual rate of the process may vary from very slow to extremely fast.

There are also some processes which require some initiation before they can proceed. But once initiated, they proceed by themselves. These processes are also regarded as spontaneous processes. Thus, the spontaneous process may be of two types:

a. Spontaneous processes where no initiation is needed.

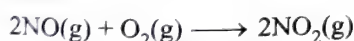
- i. Sugar dissolves in water and forms a solution.



- ii. Water keeps on evaporating from ponds, rivers, sea, and open vessels.

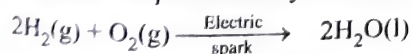


- iii. Nitric oxide (NO) and oxygen react to form nitrogen dioxide.



b. Spontaneous processes where some initiation is required.

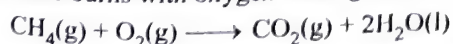
- i. Once a reaction between hydrogen and oxygen is initiated by passing electric spark through it, then it occurs itself spontaneously even at room temperature.



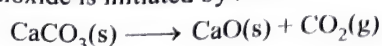
- ii. In domestic oven, coal (carbon) keeps on burning once initiated.



- iii. Methane burns with oxygen once ignited.



- iv. Heating of calcium carbonate to give calcium oxide and carbon dioxide is initiated by heat.



From the above reactions, it can be concluded that the spontaneity (or feasibility) means the inherent tendency of a process to occur of its own in a particular direction under a given set of conditions.

On the other hand, the processes that have no natural tendency to occur and are made to take place only by supplying energy continuously from outside the system are called *non-spontaneous processes*. In other words, non-spontaneous processes can be brought about by doing work. For example, a cup of tea can be made hot (reverse of natural process) by heating. But this is not a spontaneous process because an outside agency (a gas burner) has to be used. Similarly, a gas can be compressed to a smaller volume, an ink solution can be processed to obtain the ink drop, and a mixture of two gases can be separated if allowed to diffuse through a porous plug.

However, in each case, work has to be done to accomplish these changes. They do not occur spontaneously.

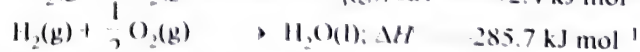
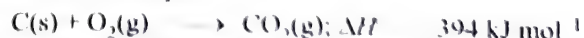
There is another important feature of the spontaneous changes. These spontaneous processes proceed till an equilibrium is achieved. For example, a cup of hot tea cools until it attains the temperature of the surroundings after which no change in temperature is observed. We say that the cup of tea and the surroundings are in thermal equilibrium. Similarly, mixing of two gases continues until each is evenly distributed throughout both the containers. Thus, all spontaneous changes proceed till equilibrium is achieved.

6.12.1 SPONTANEITY OF A PROCESS AND ENTHALPY CHANGE

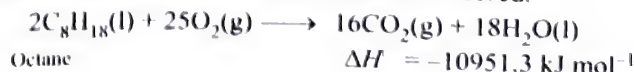
Spontaneous processes have the potential to occur in a particular direction under given set of conditions. This indicates that there must be some kind of driving force which is responsible to drag the spontaneous process in a forward direction. Let us consider some spontaneous processes in order to study the nature of this driving force. For example, falling of a ball from top of table to the ground; flowing of water from higher level to lower level.

We know that the ball or water possesses more potential energy at higher level than at lower level. This suggests that these spontaneous processes which involve macroscopic objects proceed by decrease of energy. Moreover, the state of lowest energy corresponds to the state of maximum stability. Therefore, the natural tendency of all systems in this universe to go from unstability to stability supports the fact that any process which involves a decrease in energy should have an inherent tendency to take place.

Most of the spontaneous chemical reactions are also found to be exothermic. For example:



Similarly, octane burns spontaneously in oxygen to give carbon dioxide and water and a lot of heat is evolved.



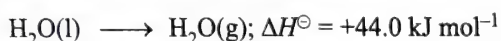
Thus, it may be concluded that all those processes which are accompanied by decrease of energy (exothermic reactions, having negative value of ΔH) occur spontaneously. In other words, the sign of ΔH may be taken as a criterion for the spontaneity of a process and decrease of enthalpy, i.e., $-\Delta H$ may be regarded as the driving force behind the spontaneous processes.

6.12.2 LIMITATIONS OF CRITERION OF DECREASE IN ENTHALPY

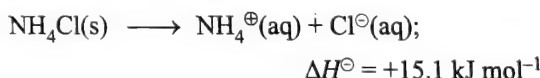
The criterion of decrease in enthalpy for the feasibility of chemical reactions fails to explain the following facts:

a. Endothermic reactions are also known to occur spontaneously. There are a number of endothermic reactions (ΔH , positive) which are known to be spontaneous. A few examples of such processes are given below:

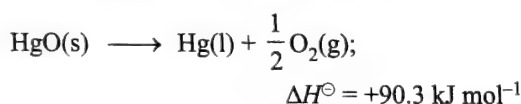
- i. Evaporation of water from an open container is an endothermic process but it is spontaneous in nature.



- ii. Dissolution of ammonium chloride in water is endothermic but occurs spontaneously.

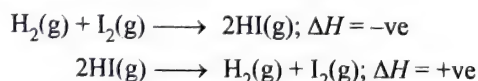


- iii. Decomposition of mercuric oxide on heating



b. Reactions do not go to completion. Most of the reactions do not go to completion even though ΔH remains negative throughout. In fact, all spontaneous chemical reactions proceed only until an equilibrium is attained.

c. Reversible reactions also occur. Most of the reactions are reversible in nature. In these reactions both the forward and the backward reactions occur simultaneously. For example, in the following reaction, the forward reaction is exothermic but the backward reaction is endothermic :



But both the reactions occur. This means that reactions with negative value of ΔH as well as positive value of ΔH are occurring simultaneously. It may be concluded that the tendency to have minimum energy, i.e., $-\Delta H$, may be the criterion for a process to be spontaneous but it cannot be the only or sole criterion.

6.12.3 RANDOMNESS OR DISORDER AND SPONTANEITY

In order to find out some other factors which may be responsible for the feasibility of the above process ($\Delta H \geq 0$), a careful study of all the above process reveals another important aspect associated with

them that all these processes proceed towards a more disordered or more random state.

In other words, nature tends to move spontaneously from a state of lower probability to one of higher probabilities, i.e., things tend to change from organised to disorganised. To illustrate what this statement means, we consider a spontaneous process of intermixing of two inert gases for which ΔH is zero. Two different inert gases, let us say helium (He) and neon (Ne), are originally contained in different glass bulbs, separated by a stopcock as shown in Fig. 6.15. To make the system as closed one, the entire system is perfectly insulated.

When the valve is opened, the intermixing of the two inert gases occurs due to diffusion into one another. As the gases are inert, there is no chemical interaction between them, the heat change during intermixing is negligible. The process of intermixing is a spontaneous process. If the process is examined critically, it is observed that when the valve is opened, both the gases are provided larger volume to occupy, i.e., each gas achieves its own most probable distribution independent of the presence of other gas. In other words, each gas occupies a large volume in the final state and, thereby, number of possible locations for the molecules of each gas is increased. This means that there is more disorder or randomness on mixing. Thus, the gases mix to achieve more randomness. Once mixed the gases cannot separate because to do so they will involve decrease in randomness due to lesser volume. Thus, it may be concluded that the process proceeds spontaneously in a direction in which the randomness or disorder of the system increases.

Thus, mixing of two gases is a spontaneous process. On the other hand, once mixed the gases cannot separate on their own and therefore it is a non-spontaneous process.

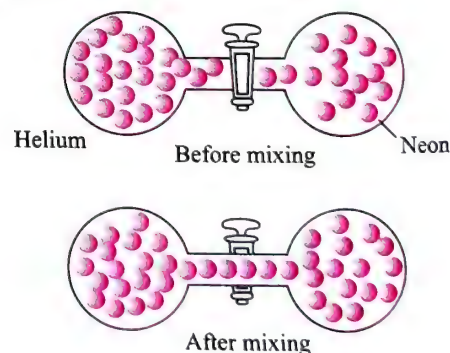
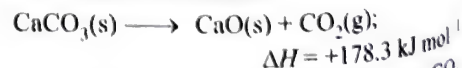


Fig. 6.15 Process of mixing of two gases. Gases mix spontaneously because of increases in randomness

Thus, the second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

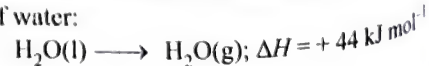
On the basis of second factor, we may also explain the spontaneity of endothermic processes.

a. Decomposition of calcium carbonate:



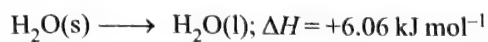
This process is spontaneous because the gaseous CO_2 produced is more random than solid calcium carbonate.

b. Evaporation of water:

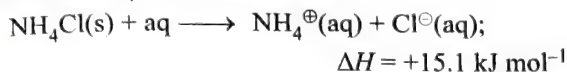


The gaseous state of a substance is more random than the liquid state. Thus, the evaporation of water is spontaneous which proceeds in the direction of more randomness.

Similarly, fusion of ice is also spontaneous because the process again proceeds in the direction of more random state, i.e., liquid state is more random in comparison to solid state.



iii. Dissolution of NH_4Cl in water:



When solid $\text{NH}_4\text{Cl(s)}$ is dissolved in water, its ions become free. Free ions move randomly in all directions. Thus, the solution is a more random state as compared to solid NH_4Cl . Thus, the process of dissolution will be spontaneous because randomness increases on dissolution.

Thus, we find that in all the above endothermic processes, there is always increase in randomness. Since the above reactions are spontaneous, the tendency to achieve maximum randomness is another factor which determines the spontaneity of a process.

Driving force as the overall tendency for a process

We have learnt that the spontaneous processes occur because of the two tendencies :

- Tendency of a system to acquire a state of minimum energy.
- Tendency of a system to acquire a state of maximum randomness.

The overall tendency for a process to take place by itself is called the driving force.

Regarding these two tendencies it is very important to keep in mind the following points:

- The two tendencies act independent of each other.
- The two tendencies may work in the same or in opposite directions in a process.

Thus, when there is no change in energy the second tendency is the governing factor i.e., reaction will be spontaneous or non-spontaneous depending upon whether randomness factor favours or opposes. On the other hand, if there is no change in randomness, the energy factor is the controlling factor. However, when both the tendencies operate simultaneously. In these cases, the significance of the magnitude of these tendencies become important. Thus, the tendency with the greater magnitude determines whether the process is feasible or not.

6.13 ENTROPY

The degree of randomness or disorder in a system may be expressed by a thermodynamic property known as entropy. Entropy may be defined as: the property of a system measures the degree of disorder or randomness in the system.

It is expressed by the symbol, S . Entropy, like internal energy and enthalpy, is a *state function* and an *extensive property*. The change in entropy during the process is represented by ΔS . Thus,

$$\Delta S = S(\text{final state}) - S(\text{initial state})$$

and for the chemical reactions

$$\Delta S = S(\text{product}) - S(\text{reactants})$$

Mathematical definition of entropy

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature (isothermally).

$$\int dS = \frac{1}{T} \int \delta q_{\text{rev}}$$

$$\text{or} \quad \Delta S = \frac{q_{\text{rev}}}{T} \quad \dots(i)$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is evolved, ΔS is negative (decrease in entropy). The value of ΔS , like ΔU and ΔH , is a definite quantity and depends on the initial and final states of the system. It is independent of the manner in which the change has been brought about, i.e., whether the change has been brought about reversibly or irreversibly.

Units of entropy and entropy change: Since entropy change is expressed as heat term divided by temperature, the units of entropy are calories per degree, i.e., cal K^{-1} . In SI units, the entropy change is expressed in terms of joules per degree, i.e., J K^{-1} . Entropy is an extensive property, i.e., it depends on the mass of the substance; hence units of entropy are expressed as cal deg^{-1} ($\text{cal K}^{-1} \text{ mol}^{-1}$) or $\text{J deg}^{-1} \text{ mol}^{-1}$ ($\text{J K}^{-1} \text{ mol}^{-1}$).

Physical meaning of entropy

The physical meaning of entropy is that entropy is a measure of degree of disorder (or randomness) of a system. The relation between entropy and disorder provides a suitable explanation for entropy change in various processes. The greater the disorder in a system, the higher is the entropy. For a substance the solid state is the state of lowest entropy, the gaseous state is the state of highest entropy and the liquid state is intermediate between the two.

Figure 6.16 shows the increase in entropy from solid to liquid to gas.

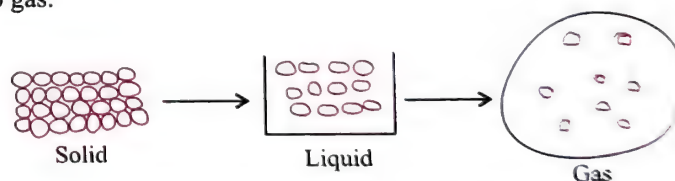


Fig. 6.16 Randomness or entropy increases

In any physical or chemical process in which the system passes from less random state to more random state, the entropy (S) increases and the value of entropy change (ΔS) will be positive.

6.13.1 ENTROPY CHANGE AND SPONTANEITY

In an isolated system, such as mixing of gases, there is no exchange of energy or matter between the system and the surroundings. However, the mixing of gases is accompanied by randomness, i.e., there is increase in entropy. Therefore, it can be stated that *for a spontaneous process in an isolated system, the change in entropy is positive, i.e., $\Delta S > 0$.*

However, if a system is not isolated, the entropy changes of both the system and the surroundings are to be taken into account because the system and surroundings together constitute

the *isolated system*. Thus, the total entropy change ($\Delta_{\text{total}}S$) is the sum of the change in entropy of the system ($\Delta_{\text{sys}}S$) and the change in the entropy of the surroundings ($\Delta_{\text{surr}}S$), i.e.,

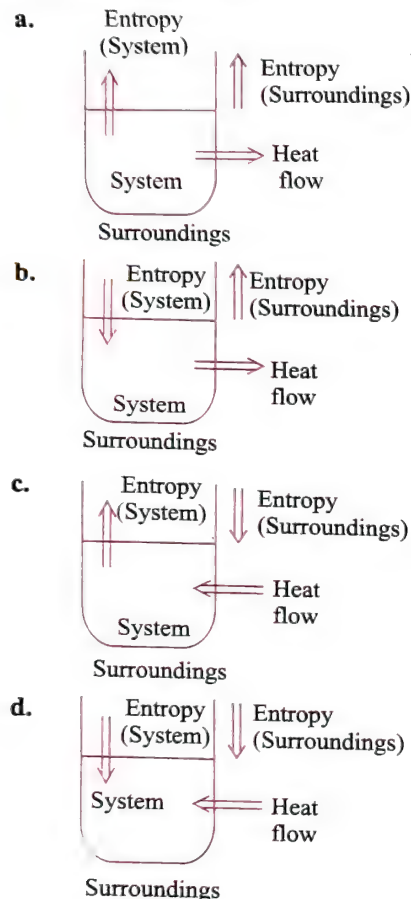
$$\Delta_{\text{total}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S$$

For a spontaneous process, $\Delta_{\text{total}}S$ must be positive, i.e.,

$$\Delta_{\text{total}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S > 0$$

$\Delta_{\text{total}}S$ is also termed as $\Delta_{\text{universe}}S$.

Visualisation of any non-isolated system can be shown as below (four cases arise):



$$\text{Case (a): } \left. \begin{array}{l} \Delta_{\text{sys}}S > 0 \\ \Delta_{\text{surr}}S > 0 \end{array} \right\} \Rightarrow \Delta_{\text{total}}S > 0$$

$$\text{Case (b): } \left. \begin{array}{l} \Delta_{\text{sys}}S < 0 \\ \Delta_{\text{surr}}S > 0 \end{array} \right\} \Rightarrow \Delta_{\text{total}}S > 0 \text{ or } < 0$$

$$\text{Case (c): } \left. \begin{array}{l} \Delta_{\text{sys}}S > 0 \\ \Delta_{\text{surr}}S < 0 \end{array} \right\} \Rightarrow \Delta_{\text{total}}S > 0 \text{ or } < 0$$

$$\text{Case (d): } \left. \begin{array}{l} \Delta_{\text{sys}}S < 0 \\ \Delta_{\text{surr}}S < 0 \end{array} \right\} \Rightarrow \Delta_{\text{total}}S < 0$$

Clearly, Case (a) is always spontaneous since change in total entropy is always positive, i.e., total entropy is increasing. Case (b) and (c) may or may not be spontaneous. Case (d) is always non-spontaneous since change in total entropy is always negative, i.e., total entropy is decreasing.

During a spontaneous process, the entropy of the system goes on increasing till the system attains the equilibrium state, i.e., entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. The mathematical condition for equilibrium is,

$$\Delta S = 0 \text{ (at equilibrium for an isolated system)}$$

If $\Delta_{\text{total}}S$ is negative, the direct process is non-spontaneous whereas the reverse process is spontaneous.

6.13.2 CHARACTERISTICS OF ENTROPY

The important characteristics of entropy are summed up below:

- Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.
- Entropy of a system is a state function. It depends upon the state variables (T, p, V, n). Thus, the change in entropy is given as

$$\Delta S = S_{\text{final state}} - S_{\text{initial state}}$$

- The change in entropy in going from one state to another is independent of the path.
- The change in entropy for a cyclic process is always zero.
- The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called the **entropy change of universe**.

$$\Delta S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S$$

- In a reversible process, $\Delta_{\text{universe}}S = 0$ and, therefore,

$$\Delta_{\text{sys}}S = -\Delta_{\text{surr}}S$$

- In an irreversible process, $\Delta_{\text{universe}}S > 0$. This means that there is increase in entropy of universe in spontaneous changes.

Notes:

- For a reversible process at equilibrium, $\Delta S = 0$.
- For an irreversible process (spontaneous) in an isolated system, $\Delta S > 0$.
- Entropy is a measure of unavailable energy.
Unavailable energy = Entropy \times Temperature.
- The entropy of universe always increases in the course of every spontaneous (natural) process i.e., $\Delta S(\text{universe}) > 0$.
- It appears that, during the stretching of rubber band entropy increases while on hard boiling of egg, entropy decreases but actually the results are reverse.
During the stretching of rubber band, the long flexible macromolecules get uncoiled. The uncoiled arrangement has more specific geometry and more order (less disorder). Thus, entropy decreases. On hard boiling of egg, denaturation of proteins occurs in which proteins from helical form changes into random coiled form. Thus, entropy increases.
- Standard enthalpy of formation and standard free energy of formation of an element is taken as zero but standard entropy of an element is not zero.
- During adiabatic expansion of a real gas, enthalpy (but not the internal energy) remains constant. It is therefore, called isenthalpic process.

8. For organic compounds belonging to the same homologous series, enthalpy of combustion increases with increase in molecular mass, but calorific value decreases.
9. A metallic element with higher atomic mass has lower specific heat and vice versa (Dulong and Petit's rule).
10. Spontaneous dissolution of gases in liquids is an exothermic process. For such a process, ΔS is always $-ve$. As such for the process to be spontaneous (ΔG to be $-ve$), ΔH has to be $-ve$ i.e., process is exothermic.
11. A non-spontaneous process with either $\Delta H = +ve$ and $\Delta S = +ve$ or $\Delta H = -ve$ and $\Delta S = -ve$, with one or more of the reactants or products in gaseous state can be made spontaneous even without changing temperature. Such a reaction can be made spontaneous by changing the pressure also.

6.14 SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics tells us whether a given process can occur spontaneously and to what extent. It also helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

The second law of thermodynamics like first law is a postulate and has not been derived from any prior concepts. It is stated in various forms. However, all the statements of second law possess same meaning.

- a. **Clausius statement:** 'It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency.'

It means that work can always be completely converted into heat but heat cannot be converted completely into work without leaving some permanent change in the system or surroundings. For example, heat produced in heat engine is never fully utilised, as part of it is always lost to surroundings or in overcoming friction, etc. Thus, it can be said that the complete conversion of heat into work is impossible without leaving some effect elsewhere.

or

It is not possible to convert heat into work without compensation.

or

All forms of energy can be converted into heat energy but heat cannot be converted into other forms of energy fully by any process.

The other similar statements are:

- b. **Thomson statement:** The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work.
- c. **Kelvin-Planck statement:** It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

- d. It is impossible to construct a heat engine of 100% thermal efficiency.

- e. **Ludwig Boltzmann statement:** In 1886, Ludwig Boltzmann gave the most useful statement of the second law of thermodynamics. Nature tends to pass from a less probable to a more probable state.

The connection between entropy and the spontaneity of a reaction or a process is expressed by the second law of thermodynamics in a number of ways.

- f. All spontaneous processes or naturally occurring processes are thermodynamically irreversible. Without the help of an external agency, a spontaneous process cannot be reversed.
- g. The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

The main ideas of the first and the second law of thermodynamics may be summarised as:

The first law states that the energy of the universe is constant whereas the second law states that the entropy of the universe is continuously increasing and tends to a maximum.

The first law deals with the conservation of energy whereas the second law tells the direction of flow of energy.

For a reversible process,

$$dS = \frac{dq}{T} \text{ or } dq = T dS$$

For an irreversible process,

$$dS > \frac{dq}{T}$$

$$\therefore dS \geq \frac{dq}{T}$$

This is the mathematical statement of the second law of thermodynamics.

6.14.1 ENTROPY AND EQUILIBRIUM STATE

During a spontaneous process, the entropy of the system goes on increasing. When the system reaches the equilibrium state, the entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. Thus, the condition for any system to achieve equilibrium state is that its entropy becomes maximum. The mathematical condition for entropy (S) to be maximum is that the change in entropy (ΔS) is zero, i.e.,

$$\Delta S = 0 \text{ at (equilibrium)}$$

Let us apply the entropy criterion to decide the feasibility of the process of conversion of water to ice, at 1 atm pressure,



The entropy changes for three different temperature 272, 273, and 274 K are given in Table 6.7.

- a. At 272 K

$$\begin{aligned} \Delta_{\text{total}} S &= \Delta_{\text{sys}} S + \Delta_{\text{surr}} S \\ &= -21.85 + 21.93 = +0.08 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Since $\Delta_{\text{total}} S$ is positive at 272 K, the freezing of liquid water to ice is spontaneous.

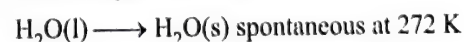


Table 6.7 Entropy changes for the transformation: $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$ at 1 atm pressure

Temperature		$\Delta_{\text{sys}}S$	$\Delta_{\text{surr}}S$	$\Delta_{\text{total}}S$
$^{\circ}\text{C}$	K	($\text{J K}^{-1} \text{mol}^{-1}$)	($\text{J K}^{-1} \text{mol}^{-1}$)	($\text{J K}^{-1} \text{mol}^{-1}$)
-1	272	-21.85	+21.93	+0.08
0	273	-21.99	+21.99	0.00
+1	274	-22.13	+22.05	-0.08

b. At 274 K

$$\Delta_{\text{total}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S$$

$$= -22.13 + 22.05 = -0.08 \text{ J K}^{-1} \text{mol}^{-1}$$

Since $\Delta_{\text{total}}S$ is negative, the freezing of water is not spontaneous at 274 K.

$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$ non-spontaneous at 274 K

But for the reverse process, $\Delta_{\text{total}}S$ will be positive, i.e., $\Delta_{\text{total}}S = 0.08 \text{ J K}^{-1} \text{mol}^{-1}$, i.e., melting is spontaneous at 274 K.

$\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$ spontaneous at 274 K

c. At 273 K

$$\Delta_{\text{total}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S = -21.99 + 21.99 = 0$$

Since $\Delta_{\text{total}}S$ is zero, the process is at equilibrium i.e., neither freezing nor melting is spontaneous. At this temperature, water and ice are in equilibrium and no net change is observed.

$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$ Equilibrium at 273 K

Thus, we observe $\Delta_{\text{total}}S$ is a criterion for spontaneity of a change.

6.14.2 CALCULATION OF CHANGES IN ENTROPY

a. Entropy change in reversible process: Consider an isothermal reversible process. In this process, let the system absorb q amount of heat from surroundings at temperature T . The increase in the entropy of the system will be

$$\Delta_{\text{sys}}S = +\frac{q}{T}$$

On the other hand, surroundings lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will

$$\Delta_{\text{surr}}S = -\frac{q}{T}$$

Total change in entropy of the process

= entropy change in system + entropy change in surrounding

$$\Delta_{\text{total}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S$$

$$= \frac{q}{T} - \frac{q}{T} = 0$$

To calculate $\Delta_{\text{sys}}S$ for a reversible process, proceed as follows:

As per definition: $\Delta S = \frac{dq_{\text{rev}}}{T}$

$$\Rightarrow T dS = dq_{\text{rev}}$$

$$\text{or } T dS = dU + (-dw)$$

[From the first law of thermodynamics]

$$\text{or } T dS = nC_V dT + P dV [dU = nC_V dT \text{ and } dw = -P dV]$$

$$\text{or } T dS = nC_V dT + \frac{nRT}{V} dV$$

$$\left[P = \frac{nRT}{V} \right]$$

$$\therefore dS = \frac{nC_V dT}{T} + \frac{nR}{V} dV$$

Integrating the above equation with appropriate limits, we get

$$\Delta_{\text{sys}}S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

...(i)

$$\text{or } \Delta_{\text{sys}}S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1 T_2}{P_2 T_1} \quad \left[\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right]$$

$$\therefore \Delta_{\text{sys}}S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + nR \ln \frac{T_2}{T_1}$$

$$\Delta_{\text{sys}}S = n \ln \frac{T_2}{T_1} (C_V + R) + nR \ln \frac{P_1}{P_2}$$

$$\Delta_{\text{sys}}S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

...(ii) [$C_P = C_V + R$]

b. Entropy change for an isothermal process

$$\Delta U = q + w$$

$$\Delta U = 0$$

(Isothermal process)

$$\Rightarrow q = -w$$

$$\text{But } w = -2.303nRT \log \frac{V_2}{V_1} \text{ or } -nRT \ln \frac{V_2}{V_1}$$

[From first law of thermodynamics]

$$\Rightarrow q = 2.303nRT \log \frac{V_2}{V_1} = nRT \ln \frac{V_2}{V_1}$$

or for a reversible process

$$q_{\text{rev}} = 2.303nRT \log \frac{V_2}{V_1} = nRT \ln \frac{V_2}{V_1}$$

$$\therefore \Delta_{\text{sys}}S = \frac{q_{\text{rev}}}{T} = \frac{nRT \ln \frac{V_2}{V_1}}{T} = \frac{2.303nRT \log \frac{V_2}{V_1}}{T}$$

$$\therefore \Delta S = nR \ln \frac{V_2}{V_1} = 2.303nR \log \frac{V_2}{V_1}$$

Also $V \propto \frac{1}{P}$ (Boyle's law)

Substituting this relation in above equation, we get

$$\Rightarrow \Delta S = 2.303nR \log \frac{P_1}{P_2} = nR \ln \frac{P_1}{P_2}$$

c. Entropy change in an isobaric process (at constant pressure)

$$dS = \frac{dq_{\text{rev}(P)}}{T} \text{ also } dq_{\text{rev}(P)} = dH$$

But $dH = C_P dT$, substituting for relationship with entropy, we get,

$$\Rightarrow dS = C_P dT/T$$

Integrating both sides

$$\int_{S_1}^{S_2} dS = C_P \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = C_p \left[\ln T \right]_{T_1}^{T_2} = C_p \ln \frac{T_2}{T_1}$$

$$\Delta S = 2.303 C_p \log \frac{T_2}{T_1} = \Delta S = C_p \ln \frac{T_2}{T_1}$$

For n moles:

$$\Delta S = n C_p \ln \frac{T_2}{T_1} = 2.303 n C_p \log \frac{T_2}{T_1}$$

d. Entropy change for Isochoric process ($\Delta V = 0$)

$$dS = \frac{dq_{\text{rev}}(P)}{T} \text{ Also } dq_{\text{rev}}(V) = dU$$

[From first law of thermodynamics]

$$\text{But } dU = C_v dT$$

$$\Rightarrow dq_v = C_v dT$$

\Rightarrow Integration both sides with proper limit, we get

$$\Delta S = C_v \left[\ln T \right]_{T_1}^{T_2} = C_v \ln \frac{T_2}{T_1}$$

$$\Delta S = 2.303 C_v \log \frac{T_2}{T_1} = C_v \ln \frac{T_2}{T_1}$$

For n moles:

$$\Delta S = n C_v \ln \frac{T_2}{T_1} = 2.303 n C_v \log \frac{T_2}{T_1}$$

e. Entropy change in adiabatic process ($q = 0$)

When the reversible process is adiabatic, there will be no heat exchange between system and surroundings, i.e., $q = 0$

$$\therefore \Delta_{\text{sys}} S = 0, \Delta_{\text{surr}} S = 0$$

$$\Delta_{\text{total}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S = 0$$

f. Entropy change in irreversible processes

Consider a system at higher temperature T_1 and its surroundings at lower temperature T_2 . q amount of heat goes irreversibly from system to surroundings.

$$\therefore \Delta_{\text{sys}} S = -\frac{q}{T_1}$$

$$\Delta_{\text{surr}} S = +\frac{q}{T_2}$$

$$\Delta_{\text{process}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S$$

$$= -\frac{q}{T_1} + \frac{q}{T_2} = q \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

But $T_1 > T_2$,

$$\therefore T_1 - T_2 = +ve$$

$$\text{or } \Delta_{\text{process}} S > 0$$

Hence, entropy increases in an irreversible process.

Table 6.8 $\Delta_{\text{sys}} S$ and $\Delta_{\text{surr}} S$ for some of the famous type of processes in thermodynamics

Process	$\Delta_{\text{sys}} S$	$\Delta_{\text{surr}} S$	Sign of $\Delta_{\text{total}} S$
Reversible Isothermal	$nR \ln \left(\frac{V_2}{V_1} \right)$	$-nR \ln \left(\frac{V_2}{V_1} \right)$	$=0$
Irreversible Isothermal	$nR \ln \left(\frac{V_2}{V_1} \right)$	$\frac{-P_{\text{ex}} \Delta V}{T}$	>0
Reversible Adiabatic	0	0	$=0$
Irreversible Adiabatic	$nC_v \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right)$	0	>0
Reversible Isobaric	$nC_p \ln \left(\frac{T_2}{T_1} \right)$	$-nC_p \ln \left(\frac{T_2}{T_1} \right)$	$=0$
Reversible Isochoric	$nC_v \ln \left(\frac{T_2}{T_1} \right)$	$-nC_v \ln \left(\frac{T_2}{T_1} \right)$	$=0$

6.14.3 ENTROPY CHANGE DURING PHASE TRANSITIONS

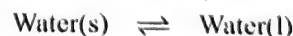
Solid, liquid, and gas are the three forms of a matter. The change of a substance from one form to another is known as *phase transformation*. Such changes occur at definite temperatures and are accompanied by entropy change. During these transformations either heat is absorbed or evolved, i.e., the entropy either increases or decreases accordingly.

The entropy change for these transformations is given by

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where q_{rev} is the heat absorbed or evolved and T is the temperature of transition. q_{rev} is actually the molar enthalpy change of the substance.

a. Entropy of fusion: It may be defined as the entropy change when 1 mol of the solid substance changes into liquid form at its melting point. For example, when ice melts as:



The change in entropy is given by

$$S'_{\text{water}} - S'_{\text{ice}} = \Delta_{\text{fus}} S' = \frac{\Delta_{\text{fus}} H'}{T_f}$$

where $\Delta_{\text{fus}} H'$ is the enthalpy of fusion and T_f is the fusion temperature.

For example, the standard enthalpy of fusion, $\Delta_{\text{fus}} H^\ominus$ at 273 K and 1 bar pressure for water is 6.0 kJ mol^{-1} .



$$\Delta_{\text{fus}} H^\ominus = 6.0 \text{ kJ mol}^{-1}$$

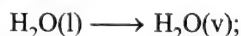
$$\begin{aligned} \therefore \Delta_{\text{fus}} S^\ominus &= \frac{q_{\text{rev}}}{T} = \frac{\Delta_{\text{fus}} H^\ominus}{T} \\ &= \frac{6.0 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}} \\ &= 21.98 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

- b. Entropy of vaporisation:** Entropy of vaporisation may be defined as the entropy change when 1 mol of a liquid changes into vapours at its boiling point. The entropy of vaporisation for a liquid at its boiling point is:

$$\Delta_{\text{vap}} S^\ominus = \frac{\Delta_{\text{vap}} H^\ominus}{T_b}$$

where $\Delta_{\text{vap}} H^\ominus$ is the standard enthalpy of vaporisation and T_b is the boiling point.

For example, standard enthalpy of vaporisation at 373 K (at 1 bar) is 40.79 kJ mol⁻¹.



$$\Delta_{\text{vap}} H^\ominus = 40.79 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \therefore \Delta_{\text{vap}} S^\ominus &= \frac{\Delta_{\text{vap}} H^\ominus}{T} \\ &= \frac{40.79 \times 10^3 \text{ J mol}^{-1}}{373 \text{ K}} \\ &= 109.356 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

- c. Entropy of sublimation:** Sublimation is a direct conversion of a solid into its vapour. Entropy of sublimation may be defined as the entropy change when 1 mol of a solid changes into vapour at a particular temperature. The entropy of sublimation at a particular temperature is

$$\Delta_{\text{sub}} S^\ominus = \frac{\Delta_{\text{sub}} H^\ominus}{T}$$

where $\Delta_{\text{sub}} H^\ominus$ is the standard enthalpy of sublimation at the temperature T ($\Delta_{\text{sub}} H^\ominus = \Delta_{\text{fus}} H^\ominus + \Delta_{\text{vap}} H^\ominus$).

QUESTIONS BASED ON IInd LAW OF THERMODYNAMICS

ILLUSTRATION 6.103

Helium weighing 16 g is expanded from 1 atm to one-tenth of its original pressure at 30°C. Calculate the change in entropy assuming it to be an ideal gas.

Sol. Since the process is an isothermal expansion of an ideal gas.

$$\Delta S = -nR \ln \frac{P_2}{P_1} \text{ or } = nR \ln \frac{P_1}{P_2}$$

$$n = \frac{16 \text{ g}}{4 \text{ g mol}^{-1}} = 4 \text{ mol}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, P_1 = 1 \text{ atm}$$

$$P_2 = \frac{1}{10} \text{ atm}$$

$$\begin{aligned} \Delta S &= (4 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \frac{1}{1/10} \\ &= 76.59 \text{ J K}^{-1} \end{aligned}$$

ILLUSTRATION 6.104

Calculate the entropy change when 2 mol of an ideal gas expand isothermally and reversibly from an initial volume of 2 dm³ to 20 dm³ at 300 K.

Sol. For an isothermal process,

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$V = 2 \text{ dm}^3, V_2 = 20 \text{ dm}^3, n = 2 \text{ mol}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \therefore \Delta S &= (2 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \frac{20 \text{ dm}^3}{2 \text{ dm}^3} \\ &= 38.294 \text{ J K}^{-1} \end{aligned}$$

ILLUSTRATION 6.105

Three moles of an ideal gas ($C_{v,m} = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$) are at 300 K and 5 dm³. If the gas is heated to 320 K and the volume changed to 10 dm³, calculate the entropy change.

Sol. The entropy changes as a function of T and V is

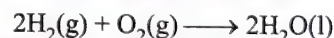
$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = (3 \text{ mol}) \times (12.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303$$

$$\begin{aligned} &\log \frac{320}{300} + (3 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \frac{10}{5} \\ &= 2.42 \text{ J K}^{-1} + 17.29 \text{ J K}^{-1} = 19.71 \text{ J K}^{-1} \end{aligned}$$

ILLUSTRATION 6.106

Determine the entropy change for the reaction given below:



at 300 K. If standard entropies of H₂(g), O₂(g), and H₂O(l) are 126.6, 201.20, and 68.0 J K⁻¹ mol⁻¹, respectively.

$$\begin{aligned} \text{Sol. } \Delta S_{\text{Reaction}} &= \Sigma S_{\text{Product}} - \Sigma S_{\text{Reactants}} \\ &= 2 \times S_{\text{H}_2\text{O}} - [2 \times S_{\text{H}_2} + S_{\text{O}_2}] \\ &= 2 \times 68 - [2 \times 126.6 + 201.20] \end{aligned}$$

$$\Delta S = -318.4 \text{ J K}^{-1}$$

ILLUSTRATION 6.107

1 mole of an ideal gas at 25°C is subjected to expand reversibly 10 times of its initial volume. Calculate the change in entropy of expansions.

$$\text{Sol. We have, } \Delta S = \frac{q_1}{T} = \frac{2.303nRT \log_{10} \frac{V_2}{V_1}}{T}$$

$$\text{Given, } n = 1, R = 8.314 \text{ J}, T = 298 \text{ K}, V_1 = V, V_2 = 10V$$

$$\therefore \Delta S = 2.303 \times 1 \times 8.314 \log_{10} \frac{10V}{V} = 19.15 \text{ J K}^{-1} \text{ mol}^{-1}$$

ILLUSTRATION 6.108

A sample of 10 g H_2O is slowly heated from 27°C to 87°C . Calculate the change in entropy during heating. (Specific heat of water = $4200 \text{ J kg}^{-1} \text{ K}^{-1}$).

Sol. $\Delta S = 2.303 \times m \times C_p \times \log \frac{T_2}{T_1}$
 $= 2.303 \times \frac{10}{1000} \times 4200 \log \frac{360}{300} = 7.65 \text{ J}$

ILLUSTRATION 6.109

I. 5 mol of an ideal gas expands reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C . Calculate the change in entropy.

- a. 70.26 J K^{-1} b. 80.55 J K^{-1}
 c. 95.73 J K^{-1} d. 107.11 J K^{-1}

II. Which of the following processes is an iso-entropic process?

- a. Isothermal process b. Adiabatic process
 c. Isobaric process d. Isochoric process

Sol.
 I. c. Entropy change (ΔS) = $2.303nR \log \frac{V_2}{V_1}$

$$= 2.303 \times 5 \times 8.314 \times \log \frac{80}{8}$$

$$= 95.73 \text{ J K}^{-1}$$

II. b. $\Delta S = \frac{Q_{\text{rev}}}{T} = \frac{0}{T} = 0$ ($Q_{\text{rev}} = 0$, in adiabatic process)

ILLUSTRATION 6.110

Calculate the entropy change when 1 mole of an ideal gas expands reversibly from an initial volume of 2 L to a final volume of 20 L at 25°C .

Sol. From the given data in the problem, we can write:

$$\Delta S_T = nR \ln \frac{V_2}{V_1}$$

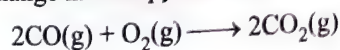
$$= 2.303 nR \log_{10} V_2/V_1$$

$$= 2.303 \times 1 \times 8.314 \times \log_{10} 20/2$$

$$= 2.303 \times 8.314 \times 1 = 19.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

ILLUSTRATION 6.111

Calculate the change in entropy for the following reaction



Given:

$$S^\circ_{\text{CO(g)}} = 197.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ_{\text{O}_2\text{(g)}} = 205.03 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ_{\text{CO}_2\text{(g)}} = 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

Sol. $\Delta S^\circ = \Sigma(S^\circ)(\text{products}) - \Sigma(S^\circ)(\text{reactants})$

$$= [2 \times S^\circ_{\text{CO}_2\text{(g)}} - 2 \times S^\circ_{\text{CO}} + S^\circ_{\text{O}_2}]$$

$$= (213.6 \times 2) - (2 \times 197.6 + 205.03)$$

$$= 427.2 - 600.23 = -173.03 \text{ J K}^{-1} \text{ mol}^{-1}$$

ILLUSTRATION 6.112

Calculate the entropy change (ΔS) when 1 mol of ice at 0°C is converted into water at 0°C . Heat of fusion of ice at 0°C is 1436 cal per mol.

Sol. Entropy change (ΔS) for the change of state of a substance is given by dividing the heat change by the absolute temperature at which the change takes place reversibly, i.e., at the melting point in this case.

$$\text{Hence, } \Delta S = \frac{q_{\text{rev}}}{T} = \frac{1436}{273} = 5.26 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

ILLUSTRATION 6.113

Predict the sign of ΔS for each of the following process:

- $\text{O}_2\text{(g)} \longrightarrow 2\text{O(g)}$
- $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \longrightarrow 2\text{NH}_3\text{(g)}$
- $\text{C(s)} + \text{H}_2\text{O(l)} \longrightarrow \text{CO(g)} + \text{H}_2\text{(g)}$
- $\text{Br}_2\text{(l)} \longrightarrow \text{Br}_2\text{(g)}$
- $\text{N}_2\text{(g, 10 atm)} \longrightarrow \text{N}_2\text{(g, 1 atm)}$
- Desalination of water
- Devitrification of glass
- Hard boiling of an egg
- $\text{C(s, graphite)} \longrightarrow \text{C(s, diamond)}$
- Stretching of rubber

Sol.

- +ve = increase in the number of gas molecules
- ve = Decrease in the number of molecules
- +ve = Increase in the number of moles
- +ve = Increase in the number of moles
- +ve = Entropy increases on expansion
- ve = Desalination is the opposite of solution
- ve = It is crystallisation of supercooled liquid
- +ve = Denaturation of protein takes place. Structure of protein change (3° to 1°) from helical structure of random configuration.
- ve = Diamond being harder solid, would be expected to have more restricted atomic motion within the crystal.
- During the stretching of rubber band the long flexible macromolecules gets uncoiled, hence more order

$$\therefore \Delta S = -ve$$

ILLUSTRATION 6.114

i. At absolute zero the entropy of a perfect crystal is zero. This statement corresponds to which law of thermodynamics?

- First law
- Second law
- Third law
- None

ii. The units of entropy are

- a. $\text{J K}^{-1} \text{mol}^{-1}$ b. $\text{K J}^{-1} \text{mol}^{-1}$
c. kJ mol^{-1} d. $\text{J K}^{-1} \text{mol}^{-2}$

Sol. a. i. c. Third law

ii. a. $\Delta S = \frac{q_{\text{rev}}}{T} = \text{J K}^{-1} \text{mol}^{-1}$

ILLUSTRATION 6.115

I. For which reaction from the following, ΔS will be maximum?

- a. $\text{Ca(s)} + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CaO(s)}$
b. $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$
c. $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
d. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO(g)}$

II. For which of these processes is the value of ΔS negative?

- i. Sugar is dissolved in water.
ii. Steam condenses on a surface.
iii. CaCO_3 is decomposed into CaO and CO_2 .
a. i only b. ii only
c. ii and iii only d. ii and iii only

III. In which of the following change entropy decreases?

- a. Crystallisation of sucrose from solution
b. Dissolving sucrose in water
c. Melting of ice
d. Vaporisation of camphor

IV. Which halogen in its standard state has the greatest absolute entropy per mole?

- a. $\text{F}_2(\text{g})$ b. $\text{Cl}_2(\text{g})$ c. $\text{Br}_2(\text{l})$ d. $\text{I}_2(\text{s})$

Sol.

I. b. $\Delta S = S_p - S_R$

$\Delta S = 2 - 1 = 1 \text{ (+ve)}$

II. b. In condensation water, vapour converts to liquid water.

III. a. Sucrose converts from liquid to solid state.

IV. b.

6.15 ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS (NERNST'S LAW)

a. The third law of thermodynamics deals with the entropies of the perfect crystalline substances at absolute zero of temperature. According to the third law of thermodynamics:

At absolute zero, the entropy of a perfectly crystalline substance is taken as zero.

Other statements of the third law of thermodynamics are:

Statement 1: 'Entropy of a solid or liquid approaches zero at the absolute zero of temperature.'

It can be mathematically expressed as

$$\lim_{T \rightarrow 0\text{K}} S \longrightarrow 0$$

Statement 2: 'It is impossible by any method, no matter how idealised it is, to reduce the temperature of any system to the absolute zero in a finite number of operation.'

This law was first formulated by German chemist Walther Nernst in 1906. Since entropy is related to disorder, therefore, according to the third law, at absolute zero, there is least disorder i.e., there is perfect order and, therefore, the entropy at perfect order is taken as zero. It may be noted that this law is true only for those substances which exist in the perfectly crystalline form at 0 K. However, if there are imperfections of any type in the perfect crystalline arrangement at 0 K, then the entropy will be larger than zero. Such entropy for imperfect crystalline arrangement at 0 K is known as residual entropy.

b. Application of the third law of thermodynamics

The third law of thermodynamics has been useful in calculating the absolute entropies of solids, liquids, and gases at different temperatures. Moreover, this law is also useful to calculate entropy changes of a chemical or physical process.

c. Calculation of Entropy at different temperature:

i. *For a solid at T K*

$$S_T - S_0 = \Delta S = \int_0^T \frac{C_p dT}{T} = C_p \ln T = 2.303 C_p \log T$$

where S_T and S_0 are the entropies at T K and 0 K respectively and $S_0 = 0$ (according to third law of thermodynamics).

The value of integral can be calculated from the graph of C_p/T against temperature (T). The area under the curve between 0 K and T K gives the value of integral and, thus, the value of S at temperature T .

When the entropy of one mole of the substance is expressed at standard state, it is called *standard molar entropy* of the substance and is denoted as S_m^\ominus . The standard entropies of various substances are given in Appendix (Table A6). The standard entropy change ($\Delta_r S^\ominus$) for a chemical reaction is the difference in molar entropy between the products and the reactants in their standard states. It may be expressed as:

$$\Delta_r S^\ominus = \left[\begin{array}{l} \text{Sum of the standard} \\ \text{entropies of products} \end{array} \right] - \left[\begin{array}{l} \text{Sum of the standard} \\ \text{entropies of reactants} \end{array} \right]$$

$$\text{or } \Delta_r S^\ominus = \sum S^\ominus (\text{products}) - \sum S^\ominus (\text{reactants})$$

$$\text{or } \Delta_r S^\ominus = \sum V_p S_m^\ominus (\text{products}) - \sum V_r S_m^\ominus (\text{reactants})$$

where V_p and V_r are stoichiometric coefficients for products and reactant, respectively.

For example, in a general reaction:



$$\Delta_r S_m^\ominus = [cS^\ominus (C) + dS^\ominus (D)] - [aS_m^\ominus (A) + bS_m^\ominus (B)]$$

- ii. For liquids and gases, the absolute entropy at a given temperature T is given by the expression

$$S = \int_0^{T_f} \frac{Cp(s)dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{Cp(l)dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^T \frac{Cp(g)dT}{T}$$

where the various terms have usual significance.

It should be noted that this law is true only for the substances which exist in perfect crystalline form at 0 K. However, if there are imperfections at 0 K, then entropy will be larger than zero.

d. Limitations of law

- Gassy solids even at 0 K has entropy greater than zero.
- Solids having mixtures of isotopes do not have zero entropy at 0 K. For example, entropy of solid chlorine is not zero at 0 K.
- Crystals of CO, N₂O, NO, H₂O, etc. do not have perfect order even at 0 K thus their entropy is not equal to zero.

ILLUSTRATION 6.116

Predict in which of the following, entropy increases/decreases:

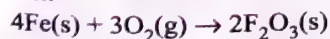
- A liquid crystallizes into a solid.
- Temperature of a crystalline solid is raised from 0 K to 115 K.
- $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$

Sol.

- After freezing, the molecules attain an ordered state and therefore, entropy decreases.
- At 0 K, the constituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore, entropy increases.
- Reactant, NaHCO₃ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.
- Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

ILLUSTRATION 6.117

For oxidation of iron.



entropy change is $-549.4 \text{ JK}^{-1} \text{ mol}^{-1}$ at 298 K. In spite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H^\ominus$ for this reaction is $-1648 \times 10^3 \text{ J mol}^{-1}$)

(NCERT Problem 6.10)

Sol. One decides the spontaneity of a reaction by considering ΔS_{total} ($\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$). For calculating ΔS_{surr} , we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T , entropy change of the surrounding is

$$\begin{aligned}\Delta S_{\text{surr}} &= -\frac{\Delta_r H^\ominus}{T} \text{ (at constant pressure)} \\ &= -\frac{(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}} \\ &= 5530 \text{ JK}^{-1} \text{ mol}^{-1}\end{aligned}$$

Thus, total entropy change for this reaction

$$\begin{aligned}\Delta_r S_{\text{total}} &= 5530 \text{ JK}^{-1} \text{ mol}^{-1} + (-549.4 \text{ JK}^{-1} \text{ mol}^{-1}) \\ &= 4980.6 \text{ JK}^{-1} \text{ mol}^{-1}\end{aligned}$$

This shows that the above reaction is spontaneous.

ILLUSTRATION 6.118

Consider the reaction for the dissolution of ammonium nitrate:



$$\Delta H = +29.8 \text{ kJ mol}^{-1}, \Delta S = 108.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the change in entropy of the surroundings and predict whether the reaction is spontaneous or not at 25°C?

Sol. The reaction is endothermic, $\Delta H = 29.8 \text{ kJ mol}^{-1}$

\therefore Entropy change in surroundings

$$\Delta_{\text{surr}} S = -\frac{\Delta_{\text{sys}} H}{T} = -\frac{29.8 \times 10^3}{298} = -100.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{\text{sys}} S = 108.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore \Delta_{\text{total}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S = 108.0 - 100.0 = 8.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

There is increase in total entropy so ammonium nitrate dissolves spontaneously.

ILLUSTRATION 6.119

I. Which of the following statement is false?

- The entropy of a substance in the liquid phase is lower than the entropy of the same substance in the gas phase
- Spontaneous reactions always occur very rapidly.
- ΔS for vaporisation of a solid is always positive.
- A spontaneous reaction in one direction is always non-spontaneous in the reversed direction.

II. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

- $\Delta_{\text{sys}} S + \Delta_{\text{surr}} S > 0$
- $\Delta_{\text{sys}} S - \Delta_{\text{surr}} S > 0$
- $\Delta_{\text{sys}} S > 0$ only
- $\Delta_{\text{surr}} S > 0$ only

III. A spontaneous process may be defined as:

- A process which is exothermic and evolves a lot of heat.
- A process which is slow and reversible.
- A process which takes place only in presence of a catalyst.
- A process that occurs without any input from the surroundings.

IV. For the reversible process, the value of ΔS is given by the expression:

- a. $\frac{q_{\text{rev}}}{T}$ b. $T - q_{\text{rev}}$ c. $q_{\text{rev}} \times T$ d. $q_{\text{rev}} - T$

Sol.

I. b.

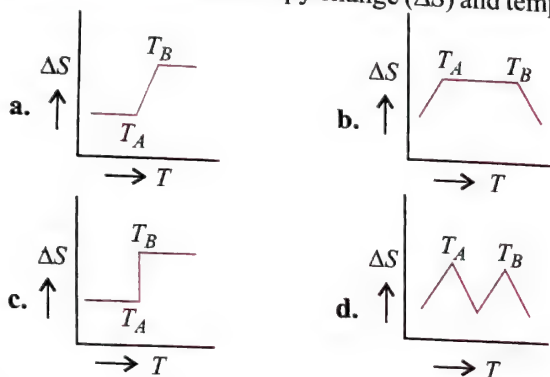
II. a. $\Delta_{\text{total}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S > 0$

III. d.

IV. a. $\Delta S = \frac{q_{\text{rev}}}{T}$

ILLUSTRATION 6.120

I. If, for a given substance, T_B is the melting point and T_A is the freezing point, then the correct variation of entropy by the graph between entropy change (ΔS) and temperature is:



- II. In thermodynamics, a process is called reversible when
 a. The surroundings and system change into each other.
 b. There is no boundary between system and surrounding.
 c. The surroundings are in equilibrium with the system.
 d. The system changes into surroundings spontaneously.

III. For spontaneous process

- a. $\Delta_{\text{total}} S = 0$ b. $\Delta_{\text{total}} S > 0$
 c. $\Delta_{\text{total}} S < 0$ d. None of these

IV. Melting point of a solid is x K and its latent heat of fusion is 600 cal mol^{-1} . The entropy change for fusion of 1 mol solid is $2 \text{ cal mol}^{-1} \text{ K}^{-1}$. The value of x will be

- a. 100 K b. 200 K c. 300 K d. 400 K

Sol.

I. a.

II. c.

III. b. $\Delta_{\text{total}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S$
 $= +\text{ve for spontaneous process}$

IV. c. $\frac{\Delta_{\text{fusion}} H^\ominus}{T_{\text{mp}}} = \Delta_{\text{fusion}} S^\ominus$

$$\frac{600}{T} = 2$$

$$T = 300 \text{ K}$$

ILLUSTRATION 6.121

I. The entropy of a crystalline substance at absolute zero on the basis of the third law of thermodynamics should be taken as

- a. 100 b. 50

c. Zero

d. Different for different substance

II. The least random state of water system is

a. Ice

b. Liquid water

c. Steam

d. Randomness is same in all

III. The value of entropy in the universe is

a. Constant

b. Decreasing

c. Increasing

d. Zero

IV. 'A spontaneous change is always accompanied by an increase in entropy'. The entropy change referred to in this statement is

a. $\Delta_{\text{sys}} S$

b. $\Delta_{\text{universe}} S$

c. $\Delta_{\text{surr}} S$

d. None of these

V. Equilibrium mixture of ice and water is held at constant pressure. On heating some ice melts. For the system

a. Entropy increases

b. Free energy increases

c. Free energy decreases

d. Entropy decreases

Sol.

I. c. Zero

II. a. Ice has solid structure and in ice water molecules are closely packed to each other.

III. c. $\Delta_{\text{surr}} S > 0$.

IV. b. $\Delta_{\text{universe}} S$

V. a. On melting, ice converts into water. In liquid state entropy increases.

QUESTIONS BASED ON IIIrd LAW OF THERMODYNAMICS

ILLUSTRATION 6.122

Calculate the entropy change accompanying the following change of state

5 mol of $\text{O}_2(27^\circ\text{C}, 1 \text{ atm}) \longrightarrow 5 \text{ mol of } \text{O}_2(117^\circ\text{C}, 5 \text{ atm})$

C_p for $\text{O}_2 = 6.95 \text{ cal deg}^{-1} \text{ mol}^{-1}$

Sol. $\Delta S_1 = \frac{q_{\text{rev}}}{T} = \frac{W_{\text{rev}}}{T} = \frac{1}{T} \times \int_{V_1}^{V_2} P dV$

$$= \frac{1}{T} \cdot nRT \int_{V_1}^{V_2} \frac{dV}{V} = nR \times 2.303 \log \frac{V_2}{V_1}$$

$$= 5 \times 1.987 \times 2.303 \log \frac{P_1}{P_2}$$

$$= 5 \times 1.987 \times 2.303 \log \frac{1}{5} = -16.0 \text{ cal deg}^{-1}$$

$\Delta S_2 =$ for the change of temperature from 27°C to 117°C

$$\begin{aligned}\Delta S_2 &= nC_P \int_{T_1}^{T_2} \frac{dT}{T} \\ &= 5 \times 6.95 \times 2.303 \log \frac{390}{300} \\ &= 5 \times 6.95 \times 2.303 \times 0.1139 \\ &= 9.12 \text{ cal deg}^{-1} \\ \Delta S &= -16.0 + 9.12 = -6.88 \text{ cal deg}^{-1}\end{aligned}$$

ILLUSTRATION 6.123

Calculate the entropy change accompanying the following change of state.



$$C_P \text{ for ice} = 9 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$C_P \text{ for H}_2\text{O} = 18 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$\text{Latent heat of fusion of ice} = 1440 \text{ cal mol}^{-1} \text{ at } 0^\circ\text{C.}$$

Sol. The total process involves three stages and entropy change can be calculated for each stage as follows:

[$\Delta S_1 \Rightarrow$ For changing 1 mole of ice from -10°C, 1 atm to 0°C, 1 atm]

$$\begin{aligned}\Delta S_1 &= \int_{-10}^0 n \cdot \frac{C_P}{T} \cdot dT \\ &= n \times C_P \times 2.303 \times \log \frac{273}{263} \\ &= 1 \times 9 \times 2.303 \times 0.0162 \\ &= 0.336 \text{ cal deg}^{-1} \text{ mol}^{-1}\end{aligned}$$

$\Delta S_2 \Rightarrow$ For melting 1 mol of ice at 0°C will be as

$$\Delta S_2 = \frac{q_{\text{rev}}}{T} = \frac{1440}{273} = 5.25 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$\Delta S_3 \Rightarrow$ For heating 1 mol of H_2O from 0°C to 10°C at 1 atm

$$\begin{aligned}\Delta S_3 &= \int_0^{10} \frac{nC_P}{T} dT \\ &= 1 \times 18 \times 2.303 \log \frac{283}{273} \\ &= 0.647 \text{ cal deg}^{-1} \text{ mol}^{-1} \\ \Delta S &= 0.336 + 5.276 + 0.647 \\ &= 6.258 \text{ cal deg}^{-1} \text{ mol}^{-1}\end{aligned}$$

ILLUSTRATION 6.124

I. How does entropy change with

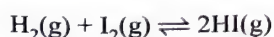
- Increase in temperature
- Decrease in pressure?

II. Is the entropy of the universe constant?

III. What is the value of change in entropy at equilibrium?

IV. Arrange water vapour, liquid water, and ice in the order of increasing entropy.

V. Do you expect ΔS to be +ve, -ve, or zero for the reaction



Sol.

- Entropy Increases with increase in temperature.
 - Entropy increases with decrease of pressure (for gases).
- No, entropy of the universe increases everyday.
- At equilibrium, the change in entropy is zero, i.e., $\Delta S = 0$ (at equilibrium).
- Ice < Liquid water < Water vapour
- ΔS should be negative because two different molecules (H_2 and I_2) would have more randomness than two same molecules (HI). Therefore, ΔS decreases.

ILLUSTRATION 6.125

- Predict the entropy change (positive/negative) in the following:
 - A liquid substance crystallises into a solid
 - Temperature of a crystal is increased
 - $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{O}_2(\text{g})$
 - $\text{N}_2(\text{g}) (1 \text{ atm}) \longrightarrow \text{N}_2(\text{g}) (0.5 \text{ atm})$
- Arrange the following in the order of increasing entropy:
 - 1 mol of $\text{H}_2\text{O}(\text{s})$ at 0°C and 1 atm pressure
 - 1 mol of $\text{H}_2\text{O}(\text{s})$ at 0°C and 1 atm pressure
 - 1 mol of $\text{H}_2\text{O}(\text{l})$ at 25°C and 1 atm pressure
 - 1 mol of $\text{H}_2\text{O}(\text{l})$ at 25°C and 0.8 atm pressure
 - 1 mol of $\text{H}_2\text{O}(\text{v})$ at 100°C and 1 atm pressure
- Predict the sign of entropy change for each of the following changes of state.
 - $\text{Hg}(\text{l}) \longrightarrow \text{Hg}(\text{g})$
 - $\text{AgNO}_3(\text{s}) \longrightarrow \text{AgNO}_3(\text{aq})$
 - $\text{I}_2(\text{g}) \longrightarrow \text{I}_2(\text{s})$
 - $\text{C}(\text{graphite}) \longrightarrow \text{C}(\text{diamond})$
- Which of the following processes are accompanied by increase of entropy:
 - Dissolution of iodine in a solvent
 - HCl is added to AgNO_3 and a precipitate of AgCl is obtained.
 - A partition is removed to allow two gases to mix.
- Place the following systems in order of increasing randomness:
 - 1 mol of a gas X
 - 1 mol of a solid X
 - 1 mol of a liquid X

Sol.

- Entropy decreases; $\Delta S = -ve$
 - Entropy increases; $\Delta S = +ve$
 - Entropy increases; $\Delta S = +ve$
 - Entropy increases; $\Delta S = +ve$
- $a < b < c < d < e$
- $\Delta S = +ve$ because liquid changes to more disordered gaseous state.
 - $\Delta S = +ve$ because aqueous solution has more disorder than solid.

- c. $\Delta S = -ve$ because gas is changing to less disordered solid.
 d. $\Delta S = +ve$ because graphite has more disorder than diamond.

IV. Increase of entropy: (a) and (c).

V. Order of increasing randomness:

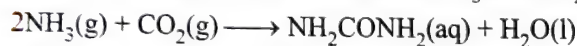
1 mol of solid X < 1 mol of liquid X < 1 mol of gas X.

CONCEPT APPLICATION EXERCISE 6.4

Subjective Type

1. 30.0 kJ of heat is required to melt 1 mol of sodium chloride. The entropy change during melting is $15.05 \text{ mol}^{-1} \text{ K}^{-1}$. Calculate the melting point of sodium chloride.

2. Calculate the change of entropy, $\Delta_r S^\ominus$ at 298 K for the reaction in which urea is formed from NH_3 and CO_2 .

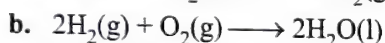
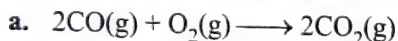


The standard entropies ($\text{J K}^{-1} \text{ mol}^{-1}$) are :

$\text{NH}_2\text{CONH}_2(\text{aq}) = 174.0$, $\text{H}_2\text{O}(\text{l}) = 69.9$

$\text{NH}_3(\text{g}) = 192.3$, $\text{CO}_2(\text{g}) = 213.7$

3. Calculate the entropy changes for the following reactions:



Entropies of different compounds are:

$\text{CO}(\text{g}) = 197.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\text{O}_2(\text{g}) = 205.03 \text{ J K}^{-1} \text{ mol}^{-1}$

$\text{CO}_2(\text{g}) = 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\text{H}_2(\text{g}) = 130.6 \text{ J K}^{-1} \text{ mol}^{-1}$

$\text{H}_2\text{O}(\text{l}) = 69.96 \text{ J K}^{-1} \text{ mol}^{-1}$.

Objective Type

4. The change in entropy of an ideal gas during reversible isothermal expansion is
 (1) Negative (2) Positive (3) Zero (4) Infinite
5. The total entropy change for a system and its surroundings increases, if the process is
 (1) Reversible (2) Irreversible
 (3) Exothermic (4) Endothermic
6. The free energy change for a reversible reaction at equilibrium is
 (1) Zero (2) Positive (3) Negative (4) None
7. Which statement(s) is/are true?
 1. S^\ominus values for all elements in their states are positive.
 2. S^\ominus values for all aqueous ions are positive.
 3. ΔS^\ominus values for all spontaneous reactions are positive.
 (1) 1 only (2) 1 and 2 only
 (3) 2 and 3 only (4) All

ANSWERS

Subjective Type

1. 2 kJ

2. $-354.4 \text{ J K}^{-1} \text{ mol}^{-1}$

3. a. -173.03 J K^{-1} , b. -326.31 J K^{-1}

Objective Type

4. (2)

5. (2)

6. (1)

7. (3)

6.16 GIBBS ENERGY AND GIBBS ENERGY CHANGE

We have seen that for a system, it is the total entropy change, $\Delta_{\text{total}} S$, which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose. We define a new thermodynamic function the Gibbs energy or Gibbs function, G .

The Gibbs energy of a system is defined as the maximum amount of energy available to a system during a process that can be converted into useful work.

In other words, it is a thermodynamic quantity which is a measure of capacity of a system to do useful work. It is denoted by symbol G and is given by

$$G = H - TS$$

where H is the enthalpy of the system, S is its entropy, and T is the absolute temperature. Gibbs energy is also called as Gibbs function.

G is an extensive property and a state function.

The change in Gibbs energy for the system, $\Delta_{\text{sys}} G$ can be written as

$$\Delta_{\text{sys}} G = \Delta_{\text{sys}} H - T \Delta_{\text{sys}} S - S_{\text{sys}} \Delta T$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta_{\text{sys}} G = \Delta_{\text{sys}} H - T \Delta_{\text{sys}} S$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T \Delta S$$

Thus, Gibbs energy change = Enthalpy change – Temperature × Entropy change, and is referred to as the Gibbs equation.

This equation is also called Gibbs–Helmholtz equation and is very useful in predicting the spontaneity of a process.

Units of ΔG

Dimensionally, if we analyse we see that ΔG has the units of energy (i.e., kJ mol^{-1} or J mol^{-1}) because both ΔH and $T \Delta S$ energy terms

$$\Delta G(\text{J mol}^{-1}) = \Delta H(\text{J mol}^{-1}) - T \Delta S(\text{J K}^{-1} \text{ mol}^{-1})$$

6.16.1 PHYSICAL SIGNIFICANCE OF GIBBS FREE ENERGY CHANGE (FREE ENERGY AND USEFUL WORK)

According to the first law of thermodynamics,

$$\Delta U = q - w \text{ (–ve sign as the work is done by system) } \dots(i)$$

Here, q is the heat absorbed by the system and w is the work done by the system while ΔU is the change in internal energy. The work (w) actually includes two types of work, i.e., $w_{\text{expansion}}$ (or $P \Delta V$) and $w_{\text{non-expansion}}$ (useful work). The two types of works can be understood by taking an example of the electrolysis of water to form $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ leading to an increase in the volume of the system. The work non-expansion (non-mechanical) is done to cause the decomposition of water while the work expansion (mechanical) is due to expansion in the volume of the system. Thus, the electrical work is called non-pressure-volume work or non-expansion work or non-mechanical work. The non-expansion work is also known as useful work. Thus,

$$\Delta U = q - w_{\text{expansion}} - w_{\text{non-expansion}} \quad \dots(\text{ii})$$

$$= q - P \Delta V - w_{\text{non-expansion}} \quad (\because w_{\text{expansion}} = P \Delta V)$$

$$\text{or } q = \Delta U + P \Delta V + w_{\text{non-expansion}} \quad \dots(\text{iii})$$

$$\text{We know that } \Delta U + P \Delta V = \Delta H$$

$$\text{or } q = \Delta H + w_{\text{non-expansion}} \quad \dots(\text{iv})$$

According to the second law of thermodynamics, for a reversible change taking place at constant temperature, T

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\text{or } q_{\text{rev}} = T \Delta S \quad \dots(\text{v})$$

Substituting in equation (iv)

$$T \Delta S = \Delta H + w_{\text{non-expansion}} \quad \dots(\text{vi})$$

$$\text{or } \Delta H - T \Delta S = -w_{\text{non-expansion}}$$

$$\text{or } \Delta G = -w_{\text{non-expansion}} \quad (\because \Delta H - T \Delta S = \Delta G)$$

$$\text{or } -\Delta G = w_{\text{non-expansion}} = w_{\text{useful work}} \quad \dots(\text{vii})$$

Thus, the decrease in Gibbs free energy is a measure of useful work or non-expansion work done by the system. The greater the free energy change, the greater is the amount of work that can be obtained from the process.

Let us take the following two conditions:

a. When useful work is done by system

$$w_{\text{useful}} = -\text{ve value}$$

$$\Rightarrow \Delta G = -\text{ve value as } \Delta G = w_{\text{useful}}$$

For any chemical reaction, $\Delta G = G_P - G_R$

$$\Rightarrow G_{\text{product}} - G_{\text{Reactant}} = -\text{ve}$$

$$\Rightarrow G_{\text{product}} < G_{\text{Reaction}}. \text{ Therefore, we can conclude that}$$

i. The capacity to do useful work by product is less than the capacity to do useful work by reactant.

ii. The product is more stable than the reactant.

Hence, according to the second law of thermodynamics, the process is a spontaneous process as every substance wants to be in the state of maximum stability.

b. When work is done on the system

$$w_{\text{useful}} = +\text{ve value}$$

$$\Rightarrow \Delta G = +\text{ve}$$

$$\Rightarrow G_P > G_R \text{ as } G_P - G_R = +\text{ve. Hence, we conclude that}$$

i. The capacity to do useful work by product is more than the capacity to do useful work by reactant.

ii. The reactant is more stable than the product.

\Rightarrow The process is non-spontaneous according to the second law of thermodynamics.

6.16.2 FREE ENERGY CHANGE AND SPONTANEITY

Let us consider a system which is not isolated from its surroundings.

In this case, total entropy change can be calculated as:

$$\Delta_{\text{total}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S \quad \dots(\text{i})$$

Let us consider the process at constant temperature and pressure. Let q_p be the amount of heat to be given by the system to the surroundings.

$$(q_p)_{\text{surr}} = -(q_p)_{\text{sys}} = -\Delta_{\text{sys}} H$$

$$\Delta_{\text{surr}} S = \frac{(q_p)_{\text{surr}}}{T} = \frac{-\Delta_{\text{sys}} H}{T} \quad \dots(\text{ii})$$

From equations (i) and (ii),

$$\Delta_{\text{total}} S = \Delta_{\text{sys}} S - \frac{\Delta_{\text{sys}} H}{T}$$

$$\text{or } T \Delta_{\text{total}} S = T \Delta_{\text{sys}} S - \Delta_{\text{sys}} H$$

$$\text{or } -T \Delta_{\text{total}} S = \Delta_{\text{sys}} H - T \Delta_{\text{sys}} S$$

According to Gibbs-Helmholtz equation,

$$\Delta G = \Delta H - T \Delta S$$

$$\therefore \Delta_{\text{sys}} G = \Delta_{\text{sys}} H - T \Delta_{\text{sys}} S \quad \dots(\text{iv})$$

From equation (iii) and (iv),

$$\Delta_{\text{sys}} G = -T \Delta_{\text{total}} S$$

We know that for spontaneous process, $\Delta_{\text{total}} S > 0$.

$$\therefore \Delta G = -\text{ve for spontaneous process}$$

Thus, for spontaneous process $T \Delta_{\text{total}} S$ should be positive or ΔG should be negative.

Case I: Let entropy and energy, both factors are favourable for a process, i.e., $\Delta H = -\text{ve}$ and $T \Delta S = +\text{ve}$

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S = (-\text{ve}) - (+\text{ve}) = -\text{ve}$$

Thus, $\Delta G = -\text{ve}$ for spontaneous process.

Case II: Let both energy and entropy factors oppose a process, i.e., $\Delta H = +\text{ve}$, $T \Delta S = +\text{ve}$

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S = (+\text{ve}) - (+\text{ve}) = +\text{ve}$$

Thus, ΔG is positive for a non-spontaneous process.

Case III: Let both tendencies be equal in magnitude but opposite, i.e.,

$$\Delta H = +\text{ve and } T \Delta S = +\text{ve and } \Delta H = T \Delta S$$

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S = 0$$

In this condition, the process is said to be at equilibrium.

These conditions are summed up in Table 6.9.

Table 6.9. Conditions for spontaneous processes, i.e., ΔG negative

ΔH	$T \Delta S$	Magnitude of the tendencies
– (Favourable)	+ (Favourable)	Any magnitude
– (Favourable)	– (Unfavourable)	$\Delta H > T \Delta S$
+ (Unfavourable)	+ (Favourable)	$T \Delta S > \Delta H$

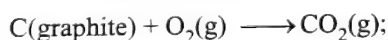
Effect of Temperature on Feasibility of a Process

As is evident from the equation: $\Delta G = \Delta H - T \Delta S$; the term $T \Delta S$ may assume larger values at higher temperatures due to increase in multiplying factor T as well as increase in randomness. But the other factor ΔH does not vary appreciably with temperature. Therefore, the Gibbs energy change (overall tendency) of a process to take place is also influenced by the temperature. The effect of temperature is different for the exothermic and the endothermic reactions as discussed below.

a. Exothermic reactions: For exothermic reactions, ΔH is always negative, and therefore, it is favourable. Now $T \Delta S$ can have either positive or negative value.

i. If $T \Delta S$ is positive, i.e., favourable, then ΔG can have only negative value and the process is spontaneous at all temperatures.

For example, in combustion of carbon at 298 K



$$\Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1}$$

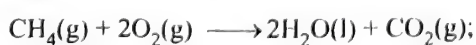
The entropy of reaction, $\Delta_r S^\ominus = 0.0029 \text{ kJ mol}^{-1}$ so that

$$\begin{aligned} \Delta_r G^\ominus &= -393.5 - 298(0.0029) \\ &= -394.36 \text{ kJ mol}^{-1} \end{aligned}$$

In this case, $\Delta_r G^\ominus$ is always negative and therefore, the reaction is always spontaneous.

ii. If $T \Delta S$ is negative i.e., unfavourable. The value of ΔG will be negative only if $\Delta H > T \Delta S$. This fact will be more predominant at lower temperatures which makes the contribution of $T \Delta S$ (opposing factor) less. When temperature is very high, $-T \Delta S$ will have large magnitude and ΔG will be positive and as such the process may not be spontaneous. But as the temperature is lowered, then the $T \Delta S$ value decreases so that its unfavourable influence is reduced. At very low temperature, the value of ΔH may become greater than the small value of $T \Delta S$ and thus, ΔG becomes negative and the process is spontaneous under these conditions. Hence, exothermic reactions are favoured by decreasing temperature.

These reactions are also *enthalpy driven*. For example, in combustion of methane (CH_4), the reaction is spontaneous because of large negative value of ΔH at 298 K.



$$\Delta_r H^\ominus = -890.3 \text{ kJ mol}^{-1}$$

$\Delta_r S^\ominus$ for the reaction has been found to be $-0.2430 \text{ kJ mol}^{-1} \text{ K}^{-1}$ so that

$$\begin{aligned} \Delta_r G^\ominus &= -890.3 - 298(-0.2430) \\ &= -817.89 \text{ kJ mol}^{-1} \end{aligned}$$

This reaction is also spontaneous at 298 K.

Thus,

- An exothermic reaction which may be non-spontaneous at high temperature because of the unfavourable entropy factor may become spontaneous at low temperature.

b. Endothermic reactions: For endothermic reactions, ΔH is positive and always opposes the process. Now,

- If $T \Delta S$ is negative and oppose the process, the ΔG will be positive and the process is always non-spontaneous.
- On the other hand, when $T \Delta S$ is positive (favourable), the value of ΔG will be negative only when $T \Delta S > \Delta H$. This fact will be more predominant at high temperatures which makes the contribution of $T \Delta S$ (favouring factor) more. At low temperature, $T \Delta S$ has small value and therefore, ΔH may be greater than $T \Delta S$. Under these conditions, ΔG may be positive and the reaction may not to be spontaneous at low temperature. As temperature increases, the term $T \Delta S$ increases while ΔH does not change appreciable. Hence, at high temperature, the magnitude of $T \Delta S$ will be quite large and will be more than ΔH so that ΔG becomes negative. This means that endotherm reactions are favoured by increasing temperature.

Thus,

- An endothermic reaction which may be non-spontaneous at low temperature because of unfavourable entropy factor may become spontaneous at high temperature.

These results are summed up in Table 6.10.

Table 6.10 Tendencies of reactions to occur in the forward direction and effect of temperature

Reaction	Sign of			Behaviour
	ΔH	$T \Delta S$	ΔG	
Exothermic	–	+	–	Spontaneous
	–	–	– (at low T)	Spontaneous
Endothermic	+	–	+	Non-spontaneous
	+	+	+	Non-spontaneous
	+	+	– (at low T)	Spontaneous

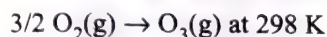
Thus, the temperature plays an important role in deciding the spontaneity of a reaction. A reaction may not spontaneous at low temperature but it becomes spontaneous at high temperature and vice versa.

Notes:

1. Gibbs energy is a state function and is an extensive property since its value depends upon the quantity of the substance.
2. During a spontaneous change the Gibbs energy decreases.
3. Change in Gibbs energy represents the maximum useful work that can be obtained from the process.

QUESTIONS BASED ON GIBBS FREE ENERGY (ΔG)**ILLUSTRATION 6.126**

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone,



if K_p for this conversion is 2.47×10^{-29} .

Sol. We know $\Delta_r G^\ominus = -2.303 RT \log K_p$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

Therefore,

$$\begin{aligned} \Delta_r G^\ominus &= -2.303(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \\ &\quad \times (298 \text{ K})(\log 2.47 \times 10^{-29}) \\ &= 163000 \text{ J mol}^{-1} \\ &= 163 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.127

Find out the value of equilibrium constant for the following reaction at 298 K.



Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is $-13.6 \text{ kJ mol}^{-1}$.

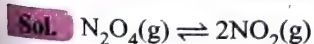
Sol. We know, $\log K = \frac{-\Delta_r G^\ominus}{2.303 RT}$

$$\begin{aligned} &= \frac{(-13.6 \times 10^3 \text{ J mol}^{-1})}{2.303 (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (298 \text{ K})} \\ &= 2.38 \end{aligned}$$

Hence $K = \text{antilog } 2.38 = 2.4 \times 10^2$

ILLUSTRATION 6.128

At 60°C , dinitrogen tetroxide is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.



If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$\begin{aligned} \chi_{\text{N}_2\text{O}_4} &= \frac{1-0.5}{1+0.5}; \quad \chi_{\text{NO}_2} = \frac{2 \times 0.5}{1+0.5} \\ p_{\text{N}_2\text{O}_4} &= \frac{0.5}{1.5} \times 1 \text{ atm}, \quad p_{\text{NO}_2} = \frac{1}{1.5} = 1 \text{ atm}. \end{aligned}$$

The equilibrium constant K_p is given by

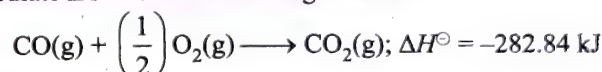
$$\begin{aligned} K_p &= \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{1.5}{(1.5)^2 (0.5)} \\ &= 1.33 \text{ atm}. \end{aligned}$$

Since

$$\begin{aligned} \Delta_r G^\ominus &= -RT \ln K_p = -2.303 RT \log k_p \\ \Delta_r G^\ominus &= (-8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (333 \text{ K}) \times (2.303) \times \\ &\quad (0.1239) \\ &= -763.8 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.129

Calculate ΔG^\ominus for the following reaction:



Given,

$$\begin{aligned} S^\ominus_{\text{CO}_2} &= 213.8 \text{ J K}^{-1} \text{ mol}^{-1}, \quad S^\ominus_{\text{CO}(\text{g})} = 197.9 \text{ J K}^{-1} \text{ mol}^{-1}, \\ S^\ominus_{\text{O}_2} &= 205.0 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

Sol. $\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$

$$\begin{aligned} &= [S^\ominus_{\text{CO}_2}] - \left[S^\ominus_{\text{CO}} + \frac{1}{2} S^\ominus_{\text{O}_2} \right] \\ &= 213.8 - \left[197.9 + \frac{1}{2} 205 \right] = -86.6 \text{ J K}^{-1} \end{aligned}$$

According to Gibbs-Helmholtz equation,

$$\begin{aligned} \Delta G^\ominus &= \Delta H^\ominus - T \Delta S^\ominus \\ &= -282.84 - 298 \times (-86.6 \times 10^{-3}) \\ &= -282.84 + 25.87 \\ &= -257.033 \text{ kJ} \end{aligned}$$

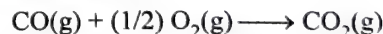
ILLUSTRATION 6.130

Show that the reaction



at 300 K is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively.

Sol. The given reaction is,



$$\begin{aligned} \Delta G^\ominus(\text{for reaction}) &= G^\ominus_{\text{CO}_2} - G^\ominus_{\text{CO}} - (1/2) G^\ominus_{\text{O}_2} \\ &= -394.4 - (-137.2) - 0 \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$

$$-257.2 = \Delta H^\ominus - 298 \times (0.094)$$

$$\text{or } \Delta H^\ominus = -288.2 \text{ kJ}$$

ΔG^\ominus is $-ve$, hence the process is spontaneous, and ΔH^\ominus is also $-ve$, hence the process is also exothermic.

ILLUSTRATION 6.131

ΔH and ΔS for the reaction:



are $30.56 \text{ kJ mol}^{-1}$ and $66.0 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Calculate the temperature at which free energy change for the reaction will be zero. Predict whether the forward reaction will be favoured above or below this temperature.

Sol. We know that, $\Delta G = \Delta H - T \Delta S$

At equilibrium, $\Delta G = 0$

so that $0 = \Delta H - T \Delta S$

$$\text{or } T = \frac{\Delta H}{\Delta S}$$

Given that $\Delta H = 30.56 \text{ kJ mol}^{-1} = 30560 \text{ J mol}^{-1}$

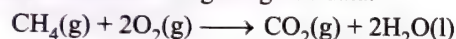
$\Delta S = 66.0 \text{ J K}^{-1} \text{ mol}^{-1}$

$$T = \frac{30560}{66} = 463 \text{ K}$$

Above this temperature, ΔG will be negative and the process will be spontaneous in forward direction.

ILLUSTRATION 6.132

Compute the standard free energy of the reaction at 27°C for the combustion of methane using the given data:



Species	CH_4	O_2	CO_2	H_2O
$\Delta_f H^\ominus$ (kJ mol^{-1})	-74.8	—	-393.5	-285.8
S^\ominus ($\text{J K}^{-1} \text{ mol}^{-1}$)	186	205	214	70

$$\begin{aligned} \text{Sol. } \Delta H^\ominus &= \Delta_f H^\ominus(\text{CO}_2) + 2\Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_f H^\ominus(\text{CH}_4) \\ &= -393.5 + 2 \times (-285.8) - (-74.8) \\ &= -890 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\ominus &= S^\ominus(\text{CO}_2) + 2S^\ominus(\text{H}_2\text{O}) - S^\ominus(\text{CH}_4) - 2S^\ominus(\text{O}_2)_{\text{sup}} \\ &= 214 + 2 \times 70 - 186 - 2 \times 205 \\ &= -242 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\ominus &= \Delta H^\ominus - T \Delta S^\ominus \\ &= -890 - 300 \times (-242 \times 10^{-3}) \\ &= -890 + 72.6 = -817.4 \text{ kJ mol}^{-1} \end{aligned}$$

ILLUSTRATION 6.133

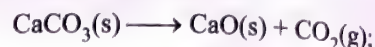
I. Which of the following statements is correct?

- ΔG is equal to ΔG^\ominus when the system is at the standard state.
- ΔG^\ominus is zero when the system is at equilibrium.
- ΔG measures how far the reaction is from equilibrium and how fast it is.
- When ΔG is positive, the reaction should proceed forward to form more product.

II. A reaction will never be spontaneous at any temperature and pressure if

- $\Delta S = +\text{ve}$, $\Delta H = +\text{ve}$
- $\Delta S = +\text{ve}$, $\Delta H = -\text{ve}$
- $\Delta S = -\text{ve}$, $\Delta H = +\text{ve}$
- $\Delta S = -\text{ve}$, $\Delta H = -\text{ve}$

III. Quick lime; (CaO) is produced by heating limestone (CaCO_3) to drive off CO_2 gas.



$$\Delta_f H^\ominus = 180 \text{ kJ mol}^{-1}, \Delta_f S^\ominus = 150 \text{ J K}^{-1}$$

Assuming that variation of enthalpy change and entropy change with temperature to be negligible, which of the following is correct?

- Decomposition of $\text{CaCO}_3\text{(s)}$ is always non-spontaneous.
- Decomposition of $\text{CaCO}_3\text{(s)}$ becomes spontaneous when temperature is less than 927°C .
- Decomposition of $\text{CaCO}_3\text{(s)}$ becomes spontaneous when temperature is greater than 1200°C .
- Decomposition of $\text{CaCO}_3\text{(s)}$ becomes spontaneous when temperature is greater than 927°C .

IV. ΔG^\ominus tells us:

- Whether a change is feasible or not.
- How far a reaction will proceed.
- About energy of activation.

Sol.

I. a.

II. c. $\Delta G = \Delta H - T \Delta S$

When $\Delta S = -\text{ve}$ and $\Delta H = +\text{ve}$, ΔG will always be $+\text{ve}$. Hence, reaction will be non-spontaneous.

III. a. $\Delta H > 0$; $\Delta S > 0 \Rightarrow$ Reaction 'may' be non-spontaneous at 25°C .

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S = 180 - 298 \times 150 \times 10^{-3} \\ &= 135.3 > 0 \end{aligned}$$

\Rightarrow Non-spontaneous.

To make it spontaneous ($\Delta G < 0$), we have to increase the temperature.

$$T_{\text{Switch}} = \frac{\Delta H}{\Delta S} = \frac{180 \times 10^3}{150} = 1200 \text{ K} = 927^\circ\text{C}$$

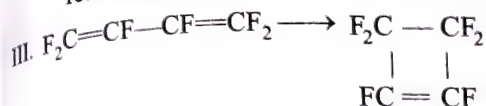
IV. a. ΔG tells about feasibility of a reaction.

ILLUSTRATION 6.134

I. Identify the correct statement for change of Gibbs energy for a system ($\Delta_{\text{sys}} G$) at constant temperature and pressure:

- if $\Delta_{\text{sys}} G = 0$, the system is still moving in a particular direction
 - if $\Delta_{\text{sys}} G < 0$, the process is not spontaneous
 - if $\Delta_{\text{sys}} G > 0$, the process is spontaneous
 - if $\Delta_{\text{sys}} G = 0$, the system has attained equilibrium
- II. Which of the following statement about above reaction is wrong?
- Heat content of product is less than of reactants.
 - For each mole of KBr(s) formed, 94.0 kcal of heat is lost.
 - Entropy of the product is lower than that of reactants.

- d. Gibbs energy of product is probably lower than that of reactants at higher temperatures.



For this reaction (ring closure), $\Delta H = -49 \text{ kJ mol}^{-1}$, $\Delta S = -40.2 \text{ J K}^{-1} \text{ mol}^{-1}$. Up to what temperature is the forward reaction spontaneous?

- a. 1492°C b. 1219°C c. 946°C d. 1080°C

Sol.

I. d. At equilibrium, $\Delta G = 0$.

II. d.

III. c. For spontaneous process

$$\Delta G = \Delta H - T \Delta S \text{ (should be negative)}$$

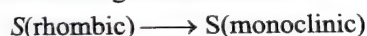
$$\therefore T > \frac{\Delta H}{\Delta S}$$

$$T > \frac{-49 \times 1000}{-40.2}$$

$$T > 1219 \text{ K, i.e., } 946^\circ\text{C}$$

ILLUSTRATION 6.135

Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs.



If $\Delta H^\circ = -276.144 \text{ J}$ at 298 K and 1 atm and $\Delta G^\circ = 75.312 \text{ J}$

- Calculate ΔS° at 298 K .
- Assume that ΔH° and ΔS° do not vary significantly with temperature, calculate T_{eq} , the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

Sol.

- a. Since $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

$$\Rightarrow \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{276.144 - 75.312}{298} = 0.674 \text{ J K}^{-1}$$

- b. Under equilibrium condition, $\Delta G = 0$

$$\Rightarrow \Delta H^\circ - T_{\text{eq}} \Delta S^\circ = 0$$

$$\Rightarrow T_{\text{eq}} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{276.144}{0.674} = 409.7 \text{ K}$$

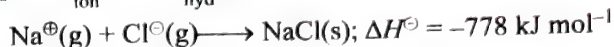
ILLUSTRATION 6.136

Calculate the free energy change when 1 mol of NaCl is dissolved in water at 298 K . Given:

- Lattice energy of $\text{NaCl} = -778 \text{ kJ mol}^{-1}$
- Hydration energy of $\text{NaCl} = -774.3 \text{ kJ mol}^{-1}$
- Entropy change at $298 \text{ K} = 43 \text{ J mol}^{-1}$

Sol. $\Delta_{\text{sol}} G^\circ = ?$

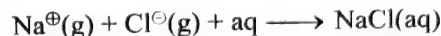
$$\Delta_{\text{sol}} H^\circ = \Delta_{\text{ion}} H^\circ + \Delta_{\text{hyd}} H^\circ$$



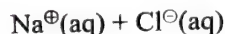
or



$$\Delta H_1 = 778 \text{ kJ mol}^{-1} \dots \text{(i)}$$

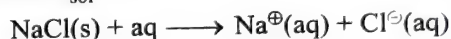


or



$$\Delta H_2 = -774.3 \text{ kJ mol}^{-1} \dots \text{(ii)}$$

To calculate $\Delta_{\text{sol}} H^\circ$



$$\Delta H^\circ = \Delta H_1 + \Delta H_2$$

$$= 778 - 774.3 = 3.7 \text{ kJ mol}^{-1} = 3700 \text{ J mol}^{-1}$$

$$\Delta_{\text{sol}} S^\circ = 43 \text{ J mol}^{-1}$$

$$\Delta_{\text{sol}} G^\circ = \Delta H^\circ - T \Delta S^\circ = 3700 - 298 \times 43 = -9114 \text{ J}$$

$$\Delta_{\text{sol}} G^\circ = -9.114 \text{ kJ}$$

6.16.3 Standard Gibbs Free Energy (ΔG°)

Just like enthalpy and internal energy, we cannot determine absolute value of Gibbs free energy. The standard free energy change can be determined and it is defined as the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted to products in their standard state. It is denoted as ΔG° ; it can be related to standard enthalpy and entropy change in the following manner:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

where ΔH° and ΔS° represent the standard enthalpy change and standard entropy change during the process, respectively.

Like that of ΔH° , ΔG° can be calculated from the standard free energies of formation of the products and the reactants.

The standard free energy of formation ($\Delta_f G^\circ$) may be defined as free energy change when 1 mol of a compound is formed from its constituent elements in their standard state.

It may be noted that like the standard enthalpy of formation ($\Delta_f H^\circ$) of an element, the standard Gibbs energy of formation of an element in its standard state is assumed to be zero.

Thus, standard Gibbs energy change of a reaction is,

$$\Delta G^\circ = \sum_f G^\circ(\text{products}) - \sum_f G^\circ(\text{reactants})$$

$$= \left[\begin{array}{c} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of products} \end{array} \right] - \left[\begin{array}{c} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of reactants} \end{array} \right]$$

Let us consider a general reaction:



$$\Delta G^\circ = \sum_f G^\circ(\text{products}) - \sum_f G^\circ(\text{reactants})$$

$$= [n_3 G^\circ(L) + n_4 G^\circ(M)] - [n_1 G^\circ(A) + n_2 G^\circ(B)]$$

ILLUSTRATION 6.137

Will the reaction,



proceed spontaneously in the forward direction of 298 K
 $\Delta_f G^\ominus \text{HI}(\text{g}) = 1.8 \text{ kJ mol}^{-1}$, $\Delta_f G^\ominus \text{H}_2\text{S}(\text{g}) = 33.8 \text{ kJ mol}^{-1}$?

Sol. $\Delta G^\ominus = \sum_f G^\ominus(\text{products}) - \sum_f G^\ominus(\text{reactants})$

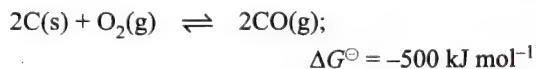
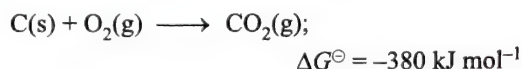
$$= [2_f G^\ominus \text{HI}(\text{g}) + _f G^\ominus \text{S}(\text{s})] - [1 \times _f G^\ominus \text{I}_2(\text{s}) + _f G^\ominus \text{H}_2\text{S}(\text{g})]$$

$$= [2 \times 1.8 + 0] - [0 + 33.8] = -30.2 \text{ kJ}$$

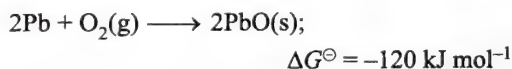
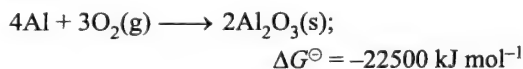
(-ve) value shows that the process is spontaneous in forward direction.

ILLUSTRATION 6.138

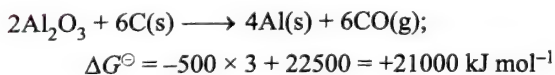
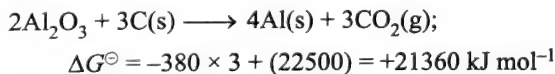
The standard Gibbs free energies for the reaction at 1773 K are given below:



Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature,

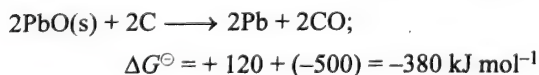
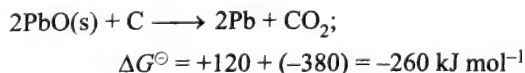


Sol. Let us consider reduction of Al_2O_3 by carbon.



Positive values of ΔG^\ominus shows that the reduction of Al_2O_3 is not possible by any of the above methods.

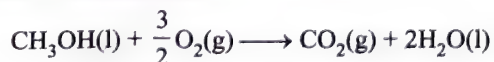
Now, let us consider the reduction of PbO .



Negative value of ΔG^\ominus shows that the process is spontaneous and PbO can be reduced by carbon.

ILLUSTRATION 6.139

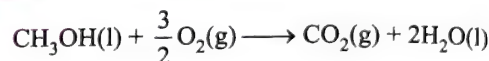
In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is



Calculate standard Gibbs free energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is -702 kJ mol^{-1} , calculate the efficiency of conversion of Gibbs energy into useful work.

$\Delta_f G^\ominus$ for CO_2 , H_2O , CH_3OH , O_2 is -394.00 , -237.00 , -166.00 , and 0 kJ mol^{-1} respectively.

Sol. The reaction for combustion of methanol is:



$$\Delta_{\text{reaction}} G^\ominus = [\Delta_f G^\ominus \text{CO}_2(\text{g}) + 2\Delta_f G^\ominus \text{H}_2\text{O}(\text{l})]$$

$$- \left[\Delta_f G^\ominus \text{CH}_3\text{OH}(\text{l}) + \frac{3}{2} \Delta_f G^\ominus \text{O}_2(\text{g}) \right]$$

$$= [-394.0 + 2(-237.00) - [-166.00 + 0]]$$

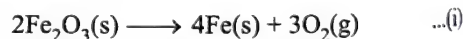
$$= -702.00 \text{ kJ mol}^{-1}$$

Efficiency of conversion of Gibbs free energy into useful work

$$= \frac{\Delta_{\text{reaction}} G^\ominus \times 100}{\Delta_{\text{reaction}} H^\ominus} = \frac{-702.00 \times 100}{-702} = 100\%$$

6.16.4 COUPLED REACTIONS

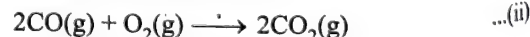
For the feasibility of a reaction, $\Delta_r G$ must be negative. There are some reactions for which the value of $\Delta_r G$ is not negative, and therefore, these reactions are not spontaneous. However, these reactions can be made spontaneous if these reactions are carried by coupling with some other reactions having very large negative Gibbs energy values so that the Gibbs energy for the two combined reactions become negative. These reactions are called coupling reactions and the Gibbs energy of the two combined reactions becomes negative. Let us consider the decomposition of iron oxide, Fe_2O_3 , into iron as:



Gibbs energy for this reaction, $\Delta_r G^\ominus = +1487.0 \text{ kJ mol}^{-1}$.

The positive value of $\Delta_r G^\ominus$ means that the reaction is non-spontaneous. This reaction can be made spontaneous by coupling with a reaction having large negative $\Delta_r G^\ominus$.

Let us consider another reaction:



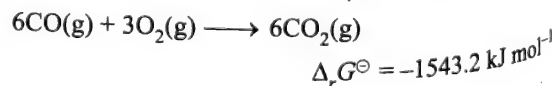
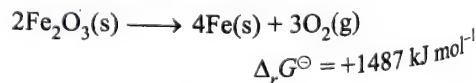
$\Delta_r G^\ominus$ for the reaction is $-514.4 \text{ kJ mol}^{-1}$.

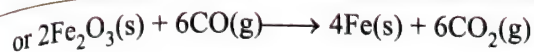
In equation (i), 3 mol of O_2 is involved so that we can write equation (ii) as:



$$\Delta_r G^\ominus = 3 \times (-514.4) = -1543.2 \text{ kJ mol}^{-1}$$

Let us combine equations (i) and (iii), we get





$$\Delta_r G^\ominus = -56.2 \text{ kJ mol}^{-1}$$

The negative value of $\Delta_r G^\ominus$ indicates that iron (III) oxide can be reduced spontaneously to iron with carbon monoxide. During the metallurgy of iron, this reaction occurs in the lower part of the blast furnace where iron oxide is reduced to iron.

The concept of coupling of two reactions is very useful in biological systems.

In our body, many biological reactions occur which involve increase in Gibbs energy ($\Delta G = +ve$). Therefore, these reactions may not be spontaneous. Adenosine triphosphate (ATP) is energy rich molecule. When ATP is hydrolysed in the presence of an enzyme it gives adenosine diphosphate (ADP) and a phosphate ion as:



$$\Delta_r G^\ominus = -31 \text{ kJ mol}^{-1}$$

This reaction is coupled with various other necessary reactions in biological systems which are otherwise not spontaneous. For example, the biosynthesis of sucrose from glucose and fructose has a $\Delta_r G^\ominus$ of $+23 \text{ kJ mol}^{-1}$. On coupling this reaction with hydrolysis of ATP, the reaction becomes spontaneous.



$$\Delta_r G^\ominus = -8 \text{ kJ mol}^{-1}$$

Therefore, ATP is regarded as centre of all activities of the cell.

6.16.5 GIBBS FREE ENERGY CHANGE AND EQUILIBRIUM

We know that for a chemical reaction to occur spontaneously, Gibbs energy change should be negative.

Now let consider a chemical reaction $A \rightleftharpoons B$ being carried in a closed vessel. As the reaction progress, the Gibbs energy decreases whether we start from reactants or products. The Gibbs energy of a reaction mixtures varies with composition of the mixture i.e., Gibbs energy decreases and composition of reaction mixtures changes gradually. Finally, a stage reaches when composition of reaction mixture becomes constant and hence the ratio $[B]/[A]$ becomes constant. This ratio is called equilibrium constant (K_{eq}). This stage refers to equilibrium state.

When we plot the Gibbs energy against its changing composition of reaction mixture with time, we get the curve as shown in Fig. 6.17. The reaction tends to proceed towards the composition at the lowest point of curve because that is the direction of decreasing Gibbs energy. The composition at the lowest point of the curve corresponds to the minimum Gibbs energy. This corresponds to equilibrium. It is clear from the figure that for a system at equilibrium, any change either in the forward reaction or reverse reaction would lead to increase in Gibbs energy. In other words, when the system attains equilibrium, any change in forward to reverse direction is not spontaneous.

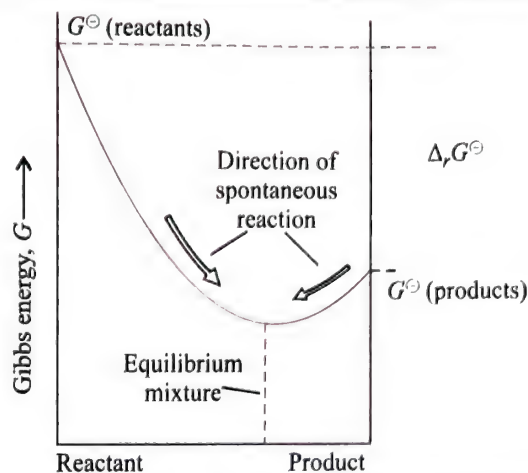


Fig. 6.17 The equilibrium composition of a reaction corresponds to minimum Gibbs energy change

The following important generalisations can be made from the above figure:

- When the Gibbs energy minimum lies very close to the products, the equilibrium composition strongly favours products. In other words, the reaction goes nearly to completion, i.e., $K_{eq} \gg 1$. This is shown in Fig. 6.18(a).
- When the Gibbs energy minimum lies very close to the reactants, the equilibrium composition favours the reactants and the reaction forms only a small amount of products. In other words, the reaction does not proceed much i.e., $K_{eq} \ll 1$. This is shown in Fig. 6.18(b).

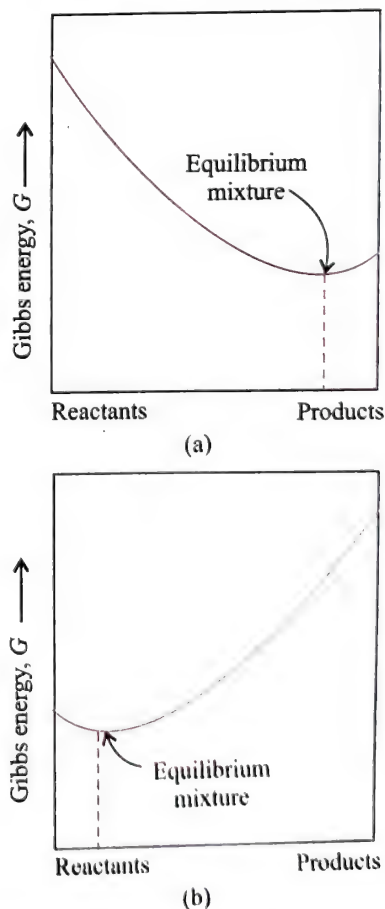


Fig. 6.18 Relative amounts of reactants and products at equilibrium

- When the Gibbs energy minimum lies approximately halfway between the reactants and the products, both reactants and

products are present in almost equal concentrations at equilibrium i.e., K is close to 1.

Relationship between standard free energy change (ΔG^\ominus) and equilibrium constant (K_{eq})

Consider a reversible reaction, $A + B \rightleftharpoons C + D$.

The Gibbs energy of reaction, ΔG is related to the composition of the reaction mixture and the standard reaction Gibbs energy, ΔG^\ominus as :

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

where ΔG is the Gibbs energy change of the reaction and ΔG^\ominus is the difference in standard Gibbs energies of formation of the products and the reactants both in their standard states. Q is the reaction quotient and $Q = \frac{[C][D]}{[A][B]}$. R is the gas constant having the value $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

If the species are gases, these concentrations are expressed in partial pressures and the reaction quotient will be Q_p and if the species are in solution, the reaction quotient will be expressed in terms of molar concentrations as Q_c .

At equilibrium, $Q = K$ and $\Delta G = 0$ because the reaction mixture has no tendency to change in either direction. Therefore, the above equation becomes:

$$0 = \Delta G^\ominus + RT \ln K$$

$$\text{or } \Delta G^\ominus = -RT \ln K$$

$$\text{or } \Delta G^\ominus = -2.303 RT \log K$$

The above equation may also be written as:

$$K = e^{-\Delta G^\ominus/RT}$$

$$\text{or } K = 10^{-\Delta G^\ominus/2.303RT}$$

This equation is very important in chemical thermodynamics because it gives relation between equilibrium constant for any process (physical or chemical) and standard Gibbs energy change. We can also conclude:

$$K < 1 \text{ when } \Delta G^\ominus > 0$$

$$K > 1 \text{ when } \Delta G^\ominus < 0$$

We also know that

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus = -RT \ln K$$

This also means that the equilibrium constant is related to ΔH^\ominus and ΔS^\ominus . For strongly endothermic reactions, ΔH^\ominus may be large and positive. In such case, value of K will be much smaller than 1. This means that the reaction is unlikely to form the products. In case of exothermic reactions, ΔH^\ominus is large and negative and ΔG^\ominus is also large and negative. In such cases, K will be larger than 1. Therefore, we generally expect strong exothermic reactions to have large K and hence these go to near completion.

Relationship between free energy change and electrical work done in a cell

Free energy change in electrochemical cells is related to the electrical work done in the cell.

ΔG and emf of the cell (E) are related by the following relation:

$$\Delta G = -nFE$$

where $F = \text{faraday} = 96500 \text{ coulomb}$

$E = \text{emf of the cell}$

$n = \text{Number of electrons involved in balanced electrochemical reaction}$

If the reactants and products are in their standard states, then

$$\Delta G^\ominus = -nFE^\ominus$$

where $E^\ominus = \text{standard emf of the cell}$

Notes:

1. Gibb's energy criteria is better than entropy criteria in determining the spontaneity. This is because the former refers to system only while the latter refers to both system and surroundings.
2. $\Delta G^\ominus = -nFE^\ominus$
where $n = \text{number of moles of electrons}$, $F = \text{Faraday}$ and $E^\ominus = \text{standard e.m.f.}$
3. $\Delta G^\ominus = -2.303 RT \log K$
where $\Delta G^\ominus = \text{standard Gibb's energy change}$ and $K = \text{equilibrium constant}$
4. The decrease in Gibb's free energy is equal to useful work done.
5. $(-\Delta G)_{T,P} = T \Delta S_{\text{total}}$
6. Standard Gibb's energies of formation of all elementary substances are taken as zero.
7. Flame temperature: It is the maximum temperature of flame zone which a system attains if the changes in the system are carried out under adiabatic conditions and at constant pressure.
8. Absolute value of internal energy, enthalpy and free energy cannot be determined whereas absolute value of entropy of any substance in any state at any temperature can be determined.

ILLUSTRATION 6.140

The emf of the cell reaction



is 1.1 V. Calculate the free energy change for the reaction. If the enthalpy of the reaction is $-216.7 \text{ kJ mol}^{-1}$, calculate the entropy change for the reaction.

Sol. $-\Delta G^\ominus = n \times F \times E^\ominus = 2 \times 96500 \times 1.1 = 212.3 \text{ kJ}$

$$\Delta G^\ominus = -212.3 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$

$$\Delta S^\ominus = \frac{\Delta H^\ominus - \Delta G^\ominus}{T} = \frac{-216.7 - (-212.3)}{298} = -0.01476 \text{ kJ K}^{-1} \text{ mol}^{-1} = -14.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

ILLUSTRATION 6.141

Calculate equilibrium constant for the following reaction:



At 25°C , $E^\ominus_{\text{cell}} = 0.47 \text{ V}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96500 \text{ C}$.

Sol. Let us apply Nernst equation at equilibrium

$$E_{\text{cell}}^{\ominus} = \frac{0.0591}{n} \log_{10} K_c$$

$$0.47 = \frac{0.0591}{2} \log_{10} K_c$$

$$K_c = \text{antilog} \left[\frac{0.47 \times 2}{0.0591} \right] = 8.5 \times 10^{15}$$

ILLUSTRATION 6.142

The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:



$$\Delta H_{300\text{ K}}^{\ominus} = -41.16 \text{ kJ mol}^{-1}$$

$$\Delta S_{300\text{ K}}^{\ominus} = -4.24 \times 10^{-2} \text{ kJ mol}^{-1}$$

$$\Delta H_{1200\text{ K}}^{\ominus} = -32.93 \text{ kJ mol}^{-1}$$

$$\Delta S_{1200\text{ K}}^{\ominus} = -2.96 \times 10^{-2} \text{ kJ mol}^{-1}$$

Calculate K_p at each temperature and predict the direction of reaction at 300 K and 1200 K, when $P_{\text{CO}} = P_{\text{CO}_2} = P_{\text{H}_2} = P_{\text{H}_2\text{O}} = 1 \text{ atm}$ at initial state.

Sol. At 300 K: $\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$

$$= -41.16 - 300 \times (-4.24 \times 10^{-2})$$

$$= -28.44 \text{ kJ}$$

Since, ΔG^{\ominus} is negative, hence reaction is spontaneous in forward direction.

$$\Delta G^{\ominus} = -2.303RT \log K_p$$

$$-28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log_{10} K_p$$

$$K_p = 8.93 \times 10^4$$

At 1200 K: $\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$

$$= -32.93 - 1200 (-2.96 \times 10^{-2})$$

$$= +2.59 \text{ kJ}$$

Positive value of ΔG^{\ominus} shows that the reaction is spontaneous in backward direction

$$\Delta G^{\ominus} = -2.303RT \log_{10} K_p$$

$$2.59 = -2.303 \times 8.314 \times 10^{-3} \times 1200 \log K_p$$

$$K_p = 0.77$$

ILLUSTRATION 6.143

Determine whether or not it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Also, calculate equilibrium constant for this reaction at 298 K.

$$\Delta_f G^{\ominus} \text{Al}_2\text{O}_3(\text{s}) = -1582 \text{ kJ mol}^{-1}$$

$$\Delta_f G^{\ominus} \text{Na}_2\text{O}(\text{s}) = -377.7 \text{ kJ mol}^{-1}$$

Sol. The reaction is:



$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(\text{Na}_2\text{O}) - \Delta_f G^{\ominus}(\text{Al}_2\text{O}_3)$$

$$= 3 \times (-377.07) - (-1582.0) = +451.21 \text{ kJ mol}^{-1}$$

Hence, the reaction cannot occur, since ΔG^{\ominus} is positive.

Also,

$$\Delta_r G^{\ominus} = 2.303RT \log K$$

$$\Rightarrow 451.21 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_{\text{eq}}$$

$$\Rightarrow \log K_{\text{eq}} = -79.0 \Rightarrow K_{\text{eq}} = 1.0 \times 10^{-79}$$

ILLUSTRATION 6.144

For the reaction:



Calculate $\Delta_r G$ of the system in a mixture of 5 mol of $\text{N}_2\text{O}_4(\text{g})$ and 5 mol of $\text{NO}_2(\text{g})$ at 298 K at a total pressure of 20 atm. Use the following data in kJ mol^{-1} :

$$\Delta_f G^{\ominus}(\text{NO}_2, \text{g}) = 50; \Delta_f G^{\ominus}(\text{N}_2\text{O}_4, \text{g}) = 100$$

Sol. We need to calculate $\Delta_r G$.

$$\text{Use : } \Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$$

So, first calculate $\Delta_r G^{\ominus}$ using:

$$\Delta_r G^{\ominus} = \sum G^{\ominus}(\text{Products}) - \sum G^{\ominus}(\text{Reactant})$$

$$= \sum (\Delta_f G^{\ominus})(\text{Products}) - \sum (\Delta_f G^{\ominus})(\text{Reactants})$$

$$[\because \text{At standard conditions: } G^{\ominus}_{\text{compounds}} = \Delta_f G^{\ominus}_{\text{compound}}]$$

$$= 2 \times \Delta_f G^{\ominus}(\text{NO}_2, \text{g}) - \Delta_f G^{\ominus}(\text{N}_2\text{O}_4, \text{g})$$

$$= 2 \times 50 - 100 = 0$$

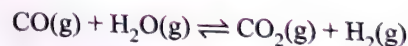
$$\text{and } \Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$$

$$= 0 + 8.314 \times 298 \ln \left(\frac{10^2}{10} \right) = 5.70 \text{ kJ mol}^{-1}$$

$$\left[\because Q = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{5}{10} \times 20 \right)^2}{\left(\frac{5}{10} \times 20 \right)} \right]$$

ILLUSTRATION 6.145

For the reaction:



$$(\Delta_r H)_{300\text{ K}} = -41.2 \text{ kJ mol}^{-1}$$

$$(\Delta_r H)_{1200\text{ K}} = -33.0 \text{ kJ mol}^{-1}$$

$$(\Delta_r S)_{300\text{ K}} = -4.2 \times 10^{-2} \text{ kJ mol}^{-1}$$

$$(\Delta_r S)_{1200\text{ K}} = -3.0 \times 10^{-2} \text{ kJ mol}^{-1}$$

Predict the direction of spontaneity of the reaction at 300 K and 1200 K. Also calculate $\log_{10} K_p$ at 300 K and 1200 K.

Sol. Using: $\Delta_r G = \Delta_r H - T \Delta_r S$

$$\text{At 300 K: } (\Delta_r G)_{300\text{ K}} = -41.2 - 300 \times (-4.2 \times 10^{-2})$$

$$= -28.6 \text{ kJ mol}^{-1}$$

$$\text{At 1200 K: } (\Delta_r G)_{1200\text{ K}} = -33.0 - 1200 \times (-3.0 \times 10^{-2})$$

$$= -3 \text{ kJ mol}^{-1}$$

Since $\Delta_r G$ is negative at 300 K and positive at 1200 K, reaction is spontaneous at 300 K and non-spontaneous at 1200 K.

$$\text{Also, } \Delta_r G^\ominus = -RT \ln K_{\text{eq}}$$

Since, $\Delta_r G$ is negative at 300 K and positive at 1200 K, reaction is spontaneous at 300 K and non-spontaneous at 1200 K.

$$\text{Also } \Delta_r G^\ominus = -RT \ln K_{\text{eq}}$$

Since $\Delta_r G^\ominus$ is not given, assume $(\Delta_r G^\ominus) = (\Delta_r G)_{300 \text{ K}}$

$$\text{At 300 K: } -28.6 = -(8.314 \times 10^{-3}) \times 300 \ln K_{\text{Eq}} \\ = 4.98$$

$$\Rightarrow \log_{10}(K_{\text{eq}})_{300 \text{ K}} \quad [\because \ln x = 2.303 \log_{10} x]$$

$$\text{and at 1200 K: } -28.6 = -(8.314 \times 10^{-3}) \times 1200 \ln K_{\text{eq}}$$

$$\Rightarrow \log_{10}(K_{\text{eq}})_{1200 \text{ K}} = 1.24$$

ILLUSTRATION 6.146

Calculate $\Delta_r G^\ominus$ at 298 K for the following reaction if the reaction mixture consists of 1 atm of N_2 , 3 atm of H_2 , and 1 atm of NH_3 .



$$\text{Sol. } \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta_r G^\ominus = -33.32 \text{ kJ}$$

$$\text{Using: } \Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

$$\text{where } Q = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{1^2}{1 \times 3^2} = \frac{1}{27};$$

$$T = 298 \text{ K}; R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Rightarrow \Delta_r G = -33.2 + (8.314 \times 10^{-3}) \times 298 \times 2.303 \log_{10} \frac{1}{27}$$

$$\Rightarrow -33.2 - 8.16 = -41.36 \text{ kJ mol}^{-1}$$

ILLUSTRATION 6.147

I. Thermodynamic efficiency of a cell is given by:

$$\text{a. } -\Delta H/\Delta G \quad \text{b. } -nFE/\Delta G \quad \text{c. } -nFE/\Delta H \quad \text{d. } -nFE^\ominus$$

II. The temperature dependence of equilibrium constant of a reaction is given by

$$\ln K_{\text{eq}} = 4.8 - \frac{2059}{T}. \text{ Find } \Delta_r G^\ominus, \Delta_r H^\ominus, \Delta_r S^\ominus.$$

III. What is the sign of ΔG^\ominus and the value of K for an electrochemical cell for which $E^\ominus_{\text{cell}} = 0.80$ volt?

$$\Delta_r G^\ominus \quad K$$

$$\text{a. } - \quad >1$$

$$\text{b. } + \quad >1$$

$$\text{c. } + \quad <1$$

$$\text{d. } - \quad <1$$

Sol.

$$\text{I. c. } -nFE/\Delta H$$

$$\text{II. Compare } \ln K_{\text{eq}} = 4.8 - \frac{2059}{T}$$

$$\text{with } \ln K_{\text{eq}} = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$$

$$\text{We have: } \frac{\Delta_r S^\ominus}{R} = 4.8$$

$$\Rightarrow \Delta_r S^\ominus = 4.8 \times 8.314 \text{ J K}^{-1} = 39.9 \text{ J K}^{-1}$$

$$\frac{\Delta_r H^\ominus}{R} = 2059$$

$$\Rightarrow \Delta_r H^\ominus = 2059 \times 8.314 \text{ J K}^{-1}$$

$$= 17.12 \text{ kJ K}^{-1}$$

$$\text{and } \Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = 17.12 - 298 \times 39.9 \times 10^{-3} \\ = 5.31 \text{ kJ K}^{-1}$$

III. a. We know that

$$\Delta G^\ominus = -nFE^\ominus$$

$$\text{When } E^\ominus = 0.80$$

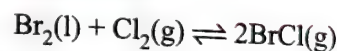
$$\text{Then } \Delta G^\ominus = -ve$$

$$\text{and } K = \text{antilog} \left(\frac{-(\Delta G^\ominus)}{-2.303 RT} \right) = \text{antilog} (+ve)$$

$$\therefore K > 1$$

ILLUSTRATION 6.148

ΔH^\ominus and ΔS^\ominus for the reaction:



at 298 K are 29.3 kJ mol^{-1} and $104.1 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively. Calculate the equilibrium constant for the reaction.

$$\text{Sol. } \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

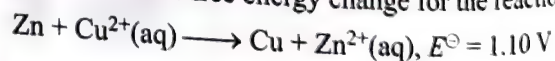
$$= 29.3 \times 10^3 - 298 \times 104.1 = -1721.8 \text{ J mol}^{-1}$$

$$\log K = -\frac{\Delta G^\ominus}{2.303 RT} = -\frac{-1721.8}{2.303 \times 8.314 \times 298} = 0.3018$$

$$K = 2.003$$

ILLUSTRATION 6.149

Calculate the standard free energy change for the reaction:



Sol. We know that

$$\Delta G^\ominus = -nFE^\ominus$$



$$n = 2, E^\ominus = 1.10 \text{ V},$$

$$F = 96500 \text{ C}$$

$$\therefore \Delta G^\ominus = -2 \times (96500 \text{ C}) \times (1.10 \text{ V})$$

$$= -212300 \text{ J} = -212.3 \text{ kJ}$$

$$(\because \text{CV} = \text{J})$$

Subjective Type

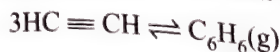
1. Calculate the Gibbs energy change on dissolving one mole of sodium chloride at 25°C.

$$\text{Lattice enthalpy} = +777.0 \text{ kJ mol}^{-1}$$

$$\text{Hydration of NaCl} = -774.0 \text{ kJ mol}^{-1}$$

$$\Delta S \text{ at } 25^\circ\text{C} = 40 \text{ J K}^{-1} \text{ mol}^{-1}$$

2. Using the following data, calculate the value of equilibrium constant for the following reaction at 298 K



Acetylene Benzene

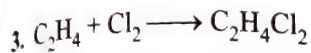
Assuming ideal behaviour

$$\Delta_f G^\ominus (\text{HC} \equiv \text{CH}) = 2.09 \times 10^5 \text{ J mol}^{-1}$$

$$\Delta_f G^\ominus (\text{C}_6\text{H}_6) = 1.24 \times 10^5 \text{ J mol}^{-1},$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Can the reaction be recommended for the synthesis of benzene?

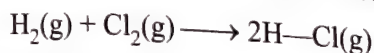


$$\Delta H = -270.6 \text{ kJ mol}^{-1} \text{ K}^{-1}; \Delta S = -139 \text{ J}$$

- a. Is the reaction favoured by entropy, enthalpy both or none?

- b. Find ΔG if $T = 300 \text{ K}$.

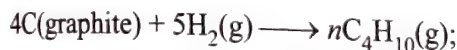
4. Calculate free energy change for the reaction:



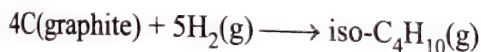
by using the bond energy and entropy data.

Bond energies of H—H, Cl—Cl, and H—Cl bonds are 435, 240, and 430 kJ mol⁻¹, respectively. Standard entropies of H₂, Cl₂, and HCl are 130.59, 222.95, and 186.68 J K⁻¹ mol⁻¹, respectively.

5. For the reaction,



$$\Delta H^\ominus = -124.73 \text{ kJ mol}^{-1}; \Delta S^\ominus = -365.8 \text{ J K}^{-1} \text{ mol}^{-1}$$



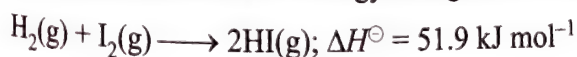
$$\Delta H^\ominus = -131.6 \text{ kJ mol}^{-1}; \Delta S^\ominus = -381.079 \text{ J K}^{-1} \text{ mol}^{-1}$$

Indicate whether normal butane can be spontaneously converted to iso-butane or not.

6. A chemical reaction cannot occur at all its

- (1) ΔH value is positive and ΔS value is negative
- (2) ΔH value is negative and ΔS value is positive
- (3) ΔH and ΔS values are negative but $\Delta H > T\Delta S$
- (4) ΔH and ΔS values are positive but $\Delta H > T\Delta S$

7. Calculate the standard free energy change for the reaction:



$$\text{Given: } S^\ominus(\text{H}_2) = 130.6 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$S^\ominus(\text{I}_2) = 116.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{and } S^\ominus(\text{HI}) = -206.8 \text{ J K}^{-1} \text{ mol}^{-1}.$$

ANSWERS

Subjective Type

1. -392 kJ mol^{-1}
2. Can be recommended
3. a. Favoured by enthalpy. b. -228.9 kJ
4. -190.9 kJ
5. The process is spontaneous.
6. (1)
7. -2.641 kJ

Solved Examples

EXAMPLE 6.1

2 mol of an ideal gas at 25°C is allowed to expand reversibly at constant temperature (isothermally) from a volume of 2 L to 10 L by reducing the pressure slowly. Calculate the work done by the gas (w), ΔU , q , and ΔH .

Sol. $w = -2.303nRT \log V_2/V_1$

$$\log V_2/V_1 = \log 10 \text{ L}/2 \text{ L} = \log 5 = 0.6990$$

$$T = 25^\circ\text{C} + 273 = 298 \text{ K}$$

$$\therefore w = -2.303 (2 \text{ mol}) (8.3143 \text{ J mol}^{-1} \text{ K}^{-1}) (298 \text{ K}) (0.6990) = -7977.1 \text{ J}$$

- a. For an isothermal reversible change, $\Delta U = 0$
- b. $\Delta U = q + w = 0$ and $q + (-7977.1 \text{ J}) = 0$; $q = 7977.1 \text{ J}$
- c. $\Delta H = \Delta U + \Delta PV = \Delta U + \Delta(nRT)$
Since R and T are constants
 $\therefore \Delta H = 0 + 0 = 0$

EXAMPLE 6.2

71 g of chlorine gas is allowed to expand freely into vacuum. Calculate w , q , ΔU , and ΔH .

Sol. $P_{\text{ex}} = 0$, $w = -P_{\text{ex}}(V_2 - V_1) = -0(V_2 - V_1) = 0$

As temperature is not given assume it as constant.

$$\therefore \Delta U = 0, \Delta U = q + w, q = 0$$

$$0 = q + 0 \quad \Delta H = 0$$

EXAMPLE 6.3

Calculate the internal energy change in each of the following cases:

- a. A system absorbs 5 kJ of heat and does 1 kJ of work.
- b. 5 kJ of work is done on the system and 1 kJ of heat is given out by the system

Sol.

- a. Here $q = +5 \text{ kJ}$, $w = +1 \text{ kJ}$

Therefore, according to the first law of thermodynamics

$$\Delta U = q - w = 5 - 1 = 4 \text{ kJ}$$

b. Here $w = -5 \text{ kJ}$, $q = -1 \text{ kJ}$

Therefore, according to first law of thermodynamics

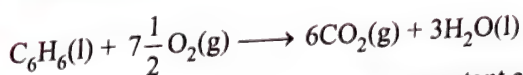
$$\Delta U = q - w = -1 - (-5) = 4 \text{ kJ}$$

i.e., the internal energy of the system increases by 4 kJ in each case.

EXAMPLE 6.4

The heat of combustion of benzene in a bomb calorimeter (i.e. constant volume) was found to be $3263.9 \text{ kJ mol}^{-1}$ at 25°C . Calculate the heat of combustion of benzene at constant pressure.

Sol. The reaction is



In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\therefore \Delta n_g = n_p - n_r = 6 - 7\frac{1}{2} = -1\frac{1}{2} = -3/2$$

Also, we are given

$$\Delta U = (\text{or } q_v) = -3263.9 \text{ kJ mol}^{-1}$$

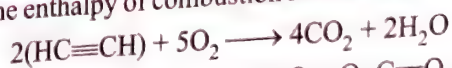
$$T = 25^\circ\text{C} = 298 \text{ K}; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{or } R = 8.314/1000 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta H (\text{or } q_p) &= \Delta U + \Delta n_g RT \\ &= -3263.9 + (-3/2) (8.314/1000) (298) \\ &= -3263.9 - 3.7 = -3267.6 \text{ kJ mol}^{-1} \end{aligned}$$

EXAMPLE 6.5

Calculate the enthalpy of combustion for the following reaction:



The bond energies of C—H, C≡C, O=O, C=O, and O—H bonds are 414, 812, 494, 707, and 463 kJ mol^{-1} , respectively.

Sol. Sum of bond energies of reactants

$$= 4 \times (\text{C—H}) + 2 \times (\text{C}\equiv\text{C}) + 5 \times (\text{O=O})$$

$$= 4 \times 414 + 2 \times 812 + 5 \times 494$$

$$= 1656 + 1624 + 2470 = 5750 \text{ kJ}$$

Sum of bond energies of products

$$= (8 \times (\text{C}=\text{O}) + 4 \times (\text{O—H})) = 8 \times 707 + 4 \times 463$$

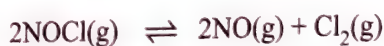
$$= 5656 + 1852 = 7508 \text{ kJ}$$

Enthalpy of combustion,

$$\Delta H = 5750 - 7508 = -1758 \text{ kJ}$$

EXAMPLE 6.6

What is the equilibrium constant, K for the following reaction at 400 K ?



Given $\Delta H^\ominus = 77.2 \text{ kJ}$, $\Delta S^\ominus = 122 \text{ J K}^{-1} \text{ mol}^{-1}$

Sol. $\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus = 7200 \text{ J} - 400 \times 122 = 28400 \text{ J}$

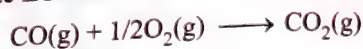
$$\Delta G^\ominus = 2.303RT \log K$$

$$28400 = -2.303 \times 8.314 \times 400 \times \log K$$

$$\log K = -3.7081 = 4.299 \text{ and } K = 1.958 \times 10^{-4}$$

EXAMPLE 6.7

Calculate ΔG^\ominus for the reaction:



Given: $\Delta H^\ominus = -282.8 \text{ kJ}$; ΔS^\ominus for CO_2 , CO , O_2 are 213.6 , 197.6 , $205 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\text{Sol. } \Delta S^\ominus = \Sigma \Delta S^\ominus_P - \Sigma \Delta S^\ominus_R$$

$$= [219.6 - 197.6 - 1/2 \times 205] = -86.5 \text{ J K}^{-1}$$

$$\text{Here } \Delta H^\ominus = -282.8 \text{ kJ (Given)} = -282800 \text{ J K}^{-1}$$

$$T = 25 + 273 = 298 \text{ K (at standard state)}$$

$$\Delta S^\ominus = -86.5 \text{ J K}^{-1} \text{ (Calculated above)}$$

$$\therefore \Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$

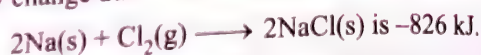
$$= -282800 - 298 \times (-86.5)$$

$$= -257023 \text{ J mol}^{-1} = 257.023 \text{ kJ mol}^{-1}$$

Since ΔG^\ominus is negative, hence the reaction is feasible.

EXAMPLE 6.8

The energy change due to the reaction



The consumption of 1 mol of Cl_2 gas contracts the system by 22.4 L at 1 atm . What is the enthalpy change of the reaction.

Sol. $W = P \Delta V = 1 \text{ atm} \times 22.4 \text{ L} = 22.4 \text{ L atm}$

$$= 22.4 \text{ L-atm} \times 101.3 \text{ J}$$

$$= 2.27 \times 10^3 = 2.27 \text{ kJ}$$

The work done on the system is to be subtracted from the energy change to get enthalpy change,

$$\Delta H = \Delta U + P \Delta V$$

$$= -826 \text{ kJ} + (-2.27 \text{ kJ}) = -828.27 \text{ kJ}$$

EXAMPLE 6.9

From N atoms of an element A , when half the atoms transfer one electron to the another atom, 405 kJ mol^{-1} of energy was found to be consumed. An additional energy of 745 kJ mol^{-1} was further required to convert all the A^\ominus ions to A^\oplus . Calculate the ionisation energy and the electron affinity of atom A in eV.

Sol. $N/2(A \longrightarrow A^\oplus)$; IE (+);

$$N/2(A \longrightarrow A^\ominus)$$
; EA (-)

$$\Rightarrow \frac{405 \times 10^3 \text{ eV}}{1.5 \times 10^{-19}} = \left(\frac{\text{IE}}{2} \times 6 \times 10^{23} - \frac{\text{EA}}{2} \times 6 \times 10^{23} \right) \dots (i)$$

$$\text{Now, } N/2(A^\ominus \longrightarrow A \longrightarrow A^\oplus)$$

$$\Rightarrow \frac{745 \times 10^3 \text{ eV}}{1.6 \times 10^{-19}} = \left(\frac{\text{IE}}{2} \times 6 \times 10^{23} - \frac{\text{EA}}{2} \times 6 \times 10^{23} \right) \dots (ii)$$

Solve for IE and EA using, equations (i) and (ii), we get

$$\text{IE} = 11.93 \text{ eV and EA} = 3.52 \text{ eV}$$

Second method:

$$1 \text{ eV} = 1 \text{ e}$$

$$y = \text{EA}$$

Solve from equations

(i) and (ii)

$$x = 1150 \text{ kJ} = 11.91 \text{ eV}$$

$$y = 340 \text{ kJ} = 3.52 \text{ eV}$$

$$(1 \text{ eV} = 96.48 \text{ kJ})$$

EXAMPLE 6.10

Using the data given below (all values are in kcal mol⁻¹ at 25°C), calculate the bond energies of C—C and C—H bonds.

ΔH° (combustion) of ethane = -372.0

ΔH° (combustion) of propane = -530.0

ΔH° for C(s) \longrightarrow C(g) = 172.0

Bond energy of H—H bond = 104.0

$\Delta_f H^\circ$ of H₂O = 68.0; $\Delta_f H^\circ$ of CO₂(g) = -94.0

Sol. Bond energies are calculated from heat of formation of a compound. Now from the data given for heats of combustion for ethane and propane, we can calculate the heats of formation of two compounds (C₂H₆ and C₃H₈) as follows:

For ethane: The equation for combustion of ethane:



$$\Delta_{\text{comb}} H^\circ = -372.0$$

From definition of ΔH° of reaction:

$$\Delta H^\circ = \Delta H_P^\circ - \Delta H_R^\circ$$

The enthalpy of a compound is the enthalpy of formation of that compound at standard conditions (i.e. $\Delta_f H^\circ$).

$$\Delta_{\text{comb}} H^\circ = [2\Delta_f H^\circ(\text{CO}_2) + 3\Delta_f H^\circ(\text{H}_2\text{O})] -$$

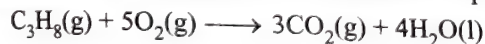
$$[\Delta_f H^\circ(\text{C}_2\text{H}_6) - 7/2\Delta_f H^\circ(\text{O}_2)]$$

$[\Delta_f H^\circ(\text{O}_2) = 0$ (as enthalpy of formation of an element in standard state is taken as zero).

$$\Rightarrow -372 = 2 \times (-94) + 3 \times (-68) - \Delta_f H^\circ(\text{C}_2\text{H}_6)$$

$$\Rightarrow \Delta_f H^\circ(\text{C}_2\text{H}_6) = -20 \text{ kcal}$$

For propane: The equation for combustion of propane.



$$\Delta_{\text{comb}} H^\circ = -530.0$$

From definition of ΔH of a reaction; $\Delta H = H_P - H_R$

$$\Delta_{\text{comb}} H^\circ = [3\Delta_f H^\circ(\text{CO}_2)] + 4\Delta_f H^\circ(\text{H}_2\text{O})]$$

$$- [\Delta_f H^\circ(\text{C}_3\text{H}_8) - \Delta_f H^\circ(\text{O}_2)]$$

$$\Rightarrow -530 = 3 \times (-94) + 4 \times (-68) - \Delta_f H^\circ(\text{C}_3\text{H}_8)$$

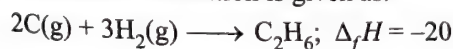
$$\Rightarrow \Delta_f H^\circ(\text{C}_3\text{H}_8) = -24 \text{ kcal}$$

Calculation of bond energies:

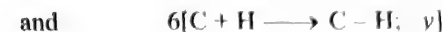
Let the energy of C—C bond = x kcal

and the bond energy of C—H bond = y kcal

For ethane, heat of formation is given as:

Bond breaking (ΔH_1):

$$\Rightarrow \Delta H_1 = 2 \times 172 + 3 \times 104 = 654$$

Bond formation (ΔH_2):

$$\Rightarrow \Delta H_2 = -(x + 6y)$$

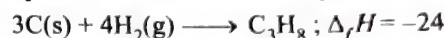
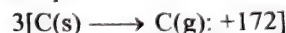
$$\Rightarrow \Delta_f H = H_1 + H_2$$

$$\Rightarrow -20 = 654 - (x + 6y)$$

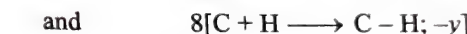
$$\Rightarrow (x + 6y) = 674$$

... (i)

For propane: heat of formation is given as

Bond breaking (H_1):

$$H_1 = 3 \times 172 + 4 \times 104 = 932$$

Bond formation (H_2):

$$\Rightarrow \Delta H_2 = -(2x + 8y)$$

$$\Rightarrow \Delta_f H = \Delta H_1 + \Delta H_2$$

$$\Rightarrow -24 = 932 - (2x + 8y)$$

$$\Rightarrow x + 4y = 478$$

... (ii)

Solving equations (i) and (ii), we get $x = 86$ and $y = 98$

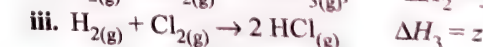
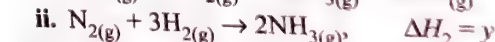
Therefore, Bond energy of C—C bond = 86 kcal

and C—H bond = 98 kcal.

EXAMPLE 6.11

Calculate the enthalpy of formation ($\Delta_f H^\circ$) of $\text{NCl}_3(\text{g})$ in terms of x , y & z .

Given:



$$\text{Sol. } \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{Cl}_2 \rightarrow \text{NCl}_3 \quad \Delta H = ?$$

$$\begin{aligned} \Delta H &= \Delta H_1 + \frac{1}{2}\Delta H_2 - \frac{3}{2}\Delta H_3 \\ &= x + \frac{1}{2}y - \frac{3}{2}z \\ &= x + \frac{1}{2}(y - 3z) \end{aligned}$$

EXAMPLE 6.12

Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol⁻¹.

Sol. Amount of hydrogen gas is

$$n_1 = \frac{PV}{RT} = \frac{(1 \text{ atm})(1 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$$= 0.04092 \text{ mol}$$

Energy consumed in dissociating hydrogen molecule

$$E_1 = (0.04092 \text{ mol})(436 \text{ kJ mol}^{-1}) = 17.84 \text{ kJ}$$

Since each hydrogen molecule gives two hydrogen atoms, the amount of hydrogen atoms will be

$$n_2 = 2n_1 = 2 \times 0.04092 \text{ mol} = 0.08184 \text{ mol}$$

Energy required to excite one mole of hydrogen atoms from the ground electronic state to the first excited state is

$$\Delta E = N_A R_H h c \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} N_A R_H h c$$

$$= \left(\frac{3}{4} \right) (6.023 \times 10^{23} \text{ mol}^{-1}) (109679 \text{ cm}^{-1}) \times$$

$$(6.626 \times 10^{-34} \text{ J}) \times (3 \times 10^8 \text{ cm s}^{-1})$$

$$= 9848.5 \text{ J mol}^{-1}$$

For exciting 0.08184 mol of hydrogen atoms, we will have

$$E_2 = (0.08184 \text{ mol})(9.8485 \text{ kJ mol}^{-1}) = 0.806 \text{ kJ}$$

Hence, the total energy required will be

$$E = E_1 + E_2 = (17.84 + 0.806) \text{ kJ} = 18.65 \text{ kJ}$$

EXAMPLE 6.13

Predict that anhydrous AlCl_3 is covalent from the data given below, ionisation energy for $\text{Al} = 5137 \text{ kJ mol}^{-1}$; $\Delta_{\text{hyd}} H$ for $\text{Al}^{3+} = -4665 \text{ kJ mol}^{-1}$; $\Delta_{\text{hyd}} H$ for $\text{Cl}^- = -381 \text{ kJ mol}^{-1}$

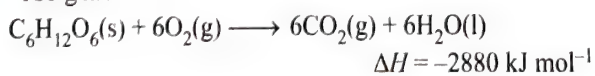
Sol. The total hydration energy of Al^{3+} and 3Cl^- ions is $\Delta H_{\text{hyd}} = \{-4665 + 3(-381)\} \text{ kJ mol}^{-1} = -5808 \text{ kJ mol}^{-1}$. The energy released is more than that required for the ionisation of Al to Al^{3+} (which is $-4665 \text{ kJ mol}^{-1}$) causing ionisation of AlCl_3 solution. Thus, the compound AlCl_3 becomes ionic in aqueous solution.

EXAMPLE 6.14

The enthalpy change involved in the oxidation of glucose is $-2880 \text{ kJ mol}^{-1}$. Twenty-five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometre, what is the maximum distance that a person will be able to walk after eating 120 g of glucose.

Sol. Molar mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)

$$= (6 \times 12 + 12 \times 1 + 6 \times 16) \text{ g mol}^{-1}$$

$$= 180 \text{ g mol}^{-1}$$


$$\text{Enthalpy consumed in muscular work} = (2880 \text{ kJ}) \left(\frac{25}{100} \right)$$

$$= 720 \text{ kJ}$$

$$\text{Amount of glucose in 120 g} = \left(\frac{120 \text{ g}}{180 \text{ g mol}^{-1}} \right)$$

$$= 0.6667 \text{ mol}$$

Enthalpy available for muscular work from 120 g of glucose

$$= (720 \text{ kJ mol}^{-1}) (0.667 \text{ mol}) = 480 \text{ kJ}$$

$$\text{Distance to which a person can move} = \left(\frac{1 \text{ km}}{100 \text{ kJ}} \right) (480 \text{ kJ})$$

$$= 4.80 \text{ km}$$

EXAMPLE 6.15

A system is provided 50 J of heat and work done on the system is 10 J. What is the change in internal energy.

Sol. $q = 50 \text{ J}$; $w = +10 \text{ J}$ (work done on the system)

$$\therefore \Delta U = q + w = 50 + 10 \Rightarrow \Delta U = 60 \text{ J}$$

EXAMPLE 6.16

How much work can be done by 100 calories of heat?

Sol. $1 \text{ cal} = 4.184 \text{ J}$

$$\therefore 100 \text{ cal} = 418.4 \text{ J}$$

$$\therefore \text{Work done} = 418.4 \text{ J}$$

EXAMPLE 6.17

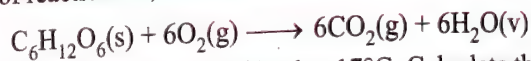
The work done by a system is 8 J, when 40 J heat is supplied to it. Calculate the increase in internal energy of system.

Sol. $w = -8 \text{ J}$; $q = 40 \text{ J}$

$$\text{From the first law; } \Delta U = q + W = 40 - 8 = 32 \text{ J}$$

EXAMPLE 6.18

Heat of reaction for,



at constant pressure is -651 kcal at 17°C . Calculate the heat of reaction at constant volume at 17°C .

Sol. $\Delta H = \Delta U + \Delta nRT$... (i)

Given $\Delta H = -651 \times 10^3 \text{ cal}$; $R = 2 \text{ cal}$;

Substituting all value in equation (i), we get

$$T = 290 \text{ K};$$

$$\Delta n = 6 + 6 - 6 = 6$$

$$\therefore -651 \times 10^3 = \Delta U + 6 \times 2 \times 290$$

$$\text{and } \Delta U = -654480 \text{ cal or } -654.48 \text{ kcal}$$

Note: For $\text{C}_6\text{H}_{12}\text{O}_6(\text{g}) + 6\text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{v})$

$\Delta n = \text{Number of products molecules} - \text{Number of reactants molecules (only in gaseous phase)} = 6 + 6 - 6 = 6$

Here, $\text{H}_2\text{O}(\text{v})$ is also in gaseous state.

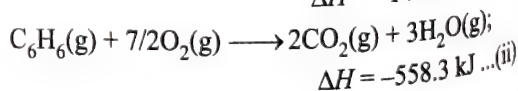
EXAMPLE 6.19

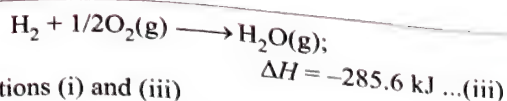
The heats of combustion of $\text{C}_2\text{H}_4(\text{g})$, $\text{C}_2\text{H}_6(\text{g})$, and $\text{H}_2(\text{g})$ are -1409.5 , -1558.3 , and -285.6 kJ , respectively. Calculate the heat of hydrogenation of ethylene.

Sol. We have to find

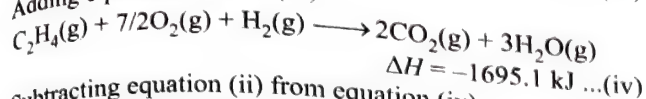


Given, $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g});$

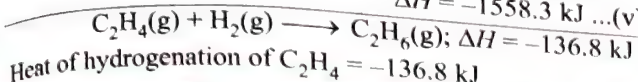
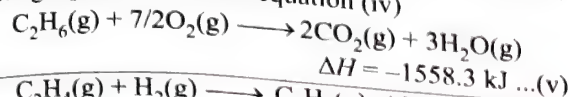
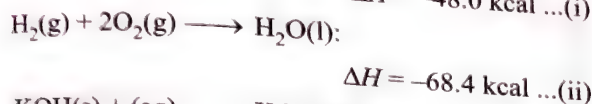
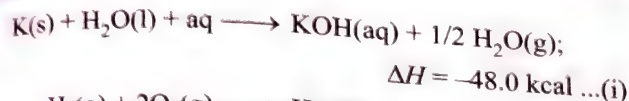
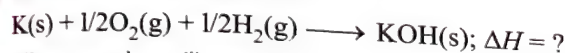
$$\Delta H = -1409.5 \text{ kJ} \dots (i)$$




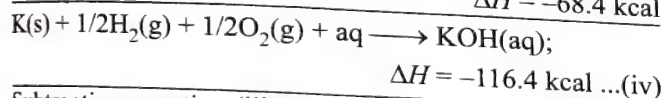
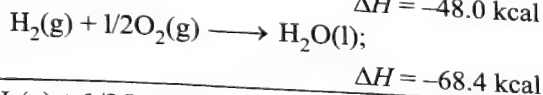
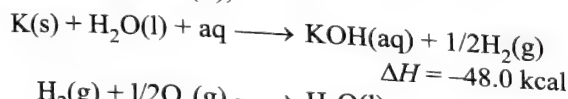
Adding equations (i) and (iii)



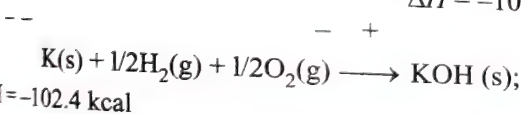
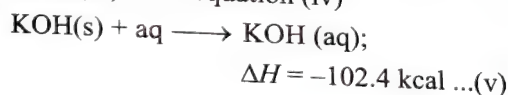
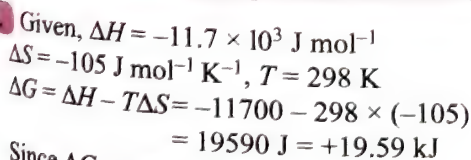
Subtracting equation (ii) from equation (iv)

Heat of hydrogenation of $\text{C}_2\text{H}_4 = -136.8 \text{ kJ}$ **EXAMPLE 6.20**Calculate heat of formation of $\text{KOH}(\text{s})$ using the following equationsWe have to evaluate ΔH for

Adding equations (i) and (ii),



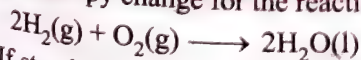
Subtracting equation (iii) from equation (iv)

**EXAMPLE 6.21**For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are $-11.7 \text{ kJ mol}^{-1}$ and $-105 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Find out whether this reaction is spontaneous or not?Since $\Delta G = +ve$

Therefore, reaction is not spontaneous.

EXAMPLE 6.22

Determine the entropy change for the reaction

at 300 K . If standard entropies of $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are 126.6 , 201.20 and $68.0 \text{ J K}^{-1} \text{ mole}^{-1}$ respectively.

Sol. $\Delta S(\text{Reaction}) = \Sigma S(\text{Product}) - \Sigma S(\text{Reactants})$

$$= 2 \times S_{\text{H}_2\text{O}} - [2 \times S_{\text{H}_2} + S_{\text{O}_2}]$$

$$= 2 \times 68 - [2 \times 126.6 + 201.20]$$

$$\Delta S = -318.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

EXAMPLE 6.23Calculate the equilibrium constant for the reaction given below at 400 K , if $\Delta H^\ominus = 77.2 \text{ kJ mole}^{-1}$ and $\Delta S^\ominus = 122 \text{ J K}^{-1} \text{ mole}^{-1}$.

Sol. $\Delta H^\ominus = 77.2 \text{ kJ mol}^{-1}$; $\Delta S^\ominus = 122 \text{ J K}^{-1} \text{ mol}^{-1}$

$$T = 400 \text{ K}$$

$$\therefore \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$\Delta G^\ominus = 77200 - 400 \times 122 = 28400 \text{ J}$$

Also we have, $-\Delta G^\ominus = 2.303RT \log K_c$,where K is equilibrium constant

$$\therefore -28400 = 2.303 \times 8.314 \times 400 \log K_c$$

$$\therefore K_c = 1.958 \times 10^{-4}$$

EXAMPLE 6.24

- A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20000 kJ of energy per day for cooking, how long will the cylinder last? Given that the heat of combustion of butane is 2658 kJ mol^{-1} .
- If the air supply of the burner is insufficient (i.e. you have a yellow instead of a blue flame), a portion of the gas escapes without combustion. Assuming that 33% of the gas is wasted due to this inefficiency, how long would the cylinder last?

Sol.

- 1 mol of butane, i.e., C_4H_{10} ($=58 \text{ g}$) gives heat $= 2658 \text{ kJ}$

$$\therefore 58 \text{ g of } \text{C}_4\text{H}_{10} \text{ gives heat} = 2658 \text{ kJ}$$

$$11.2 \times 1000 \text{ g gives}$$

$$\Rightarrow \frac{2658 \times 11.2 \times 1000}{58} \Rightarrow 513268.96 \text{ kJ}$$

$$\therefore 20000 \text{ kJ of heat is required for 1 day.}$$

$$\therefore 513268.96 \text{ kJ of heat is required for}$$

$$= \frac{513268.96}{20000} = 25.66 \text{ days}$$

$$\approx 26 \text{ days}$$

- 33% of heat is wasted, therefore, 67% of heat is utilised.

$$\therefore \text{Heat utilised} = \frac{513268.96 \times 67}{100} = 343890 \text{ kJ}$$

$$\text{Number of days} = \frac{343890}{20000} = 17.19 \text{ days}$$

$$\approx 17 \text{ days.}$$

EXAMPLE 6.25

The energy released in the neutralisation of H_2SO_4 and KOH is 59.1 kJ. Calculate the value ΔH for the reaction



Sol. $\Delta H = -2 \times 59.1 = -118.2 \text{ kJ}$

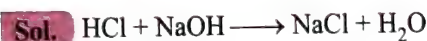
EXAMPLE 6.26

What is the calorific or fuel value of 1 kg of CH_4 ?

Sol. Calorific value/kg = $\frac{890}{16} \times 1000 = 55625 \text{ kJ kg}^{-1}$

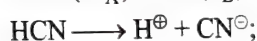
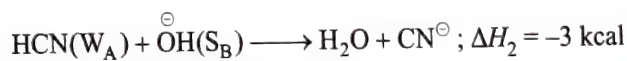
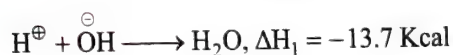
EXAMPLE 6.27

Heat of neutralisation between HCl and NaOH is 13.7 kcal and between HCN and NaOH is 3 kcal at 45°C . Calculate the heat of ionisation of HCN



$S_A \quad S_B$

or

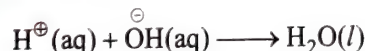


$$\therefore \Delta H = \Delta H_2 - \Delta H_1 \\ = -3 - (-13.7) = 10.7 \text{ kcal}$$

EXAMPLE 6.28

Enthalpy of neutralisation of acetic acid by NaOH is $-50.6 \text{ kJ mol}^{-1}$. Calculate ΔH for ionisation of CH_3COOH . Given, the heat of neutralisation of a strong acid with a strong base is $-55.9 \text{ kJ mol}^{-1}$.

Sol. The neutralisation of a strong acid by a strong base is represented by:

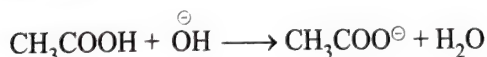


$$\Delta H = -55.9 \text{ kJ} \quad \dots(\text{i})$$

We have to calculate:



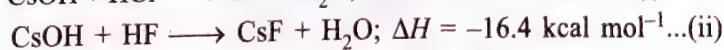
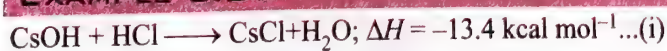
Given:



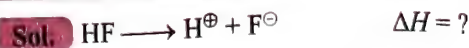
$$\Delta H_2 = -50.6 \quad \dots(\text{ii})$$

Operate: $\therefore (\text{ii}) - (\text{i})$

$$\therefore \Delta H = \Delta H_2 - \Delta H_1 \\ = -50.6 - (-55.9) = 5.3 \text{ kJ mol}^{-1}$$

EXAMPLE 6.29

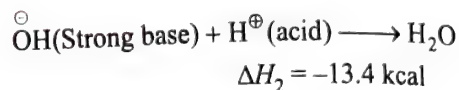
Calculate ΔH for the ionisation of HF in H_2O .



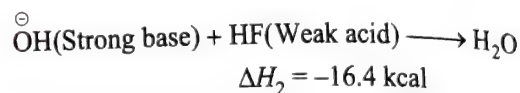
From equation (i), we get



or



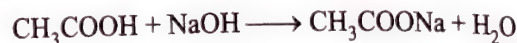
From equation (ii), we get



$$\Delta H = \Delta H_2 - \Delta H_1 \\ = -16.4 - (-13.4) = -3.0 \text{ kcal}$$

EXAMPLE 6.30

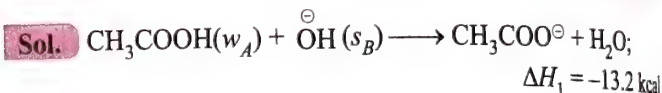
Calculate heat of dissociation for acetic acid from the following data:



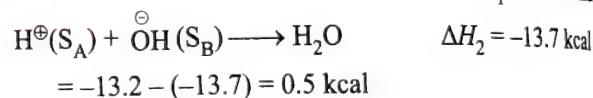
$$\Delta H = -13.2 \text{ kcal}$$



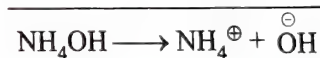
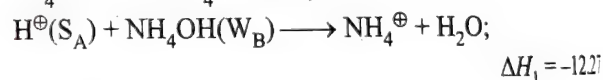
Also calculate heat of dissociation for NH_4OH if



$$\Delta H_1 = -13.2 \text{ kcal}$$



Similarly, for NH_4OH :



$$\Delta H = \Delta H_1 - \Delta H_2 = -12.7 - (-13.7) = 1.43 \text{ cal}$$

EXAMPLE 6.31

Calculate the resonance energy of NO_2 ($:\text{O}-\text{N}=\text{O}:$)

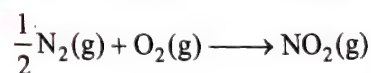
The measured enthalpy formation of NO_2 ($\Delta_f H^{\ominus}$) is 34 kJ mol^{-1} . The bond energies given are:

$$\text{N}-\text{O} \Rightarrow 222 \text{ kJ mol}^{-1}$$

$$\text{N} \equiv \text{N} \Rightarrow 946 \text{ kJ mol}^{-1}$$

$$\text{O}=\text{O} \Rightarrow 498 \text{ kJ mol}^{-1}$$

$$\text{N}=\text{O} \Rightarrow 607 \text{ kJ mol}^{-1}$$



$$\Delta_f H_{\text{cal}} = (\text{BE of Reactant} - \text{BE of Products})$$

$$\begin{aligned}
 &= \left(\frac{1}{2} \text{BE of N}_2 + \text{BE of O}_2 \right) \\
 &\quad - \left(\frac{1}{2} \text{BE of N=O} + \text{BE of N-O} \right) \\
 &= \left(\frac{1}{2} \times 946 + 498 \right) - (607 + 222) \\
 &= 971 - 829 = 142 \text{ kJ}
 \end{aligned}$$

$$\Delta H_{\text{(observed)}} = 34 \text{ kJ}$$

$$\therefore \text{R.E.} = 34 - 142 = -108 \text{ kJ}$$

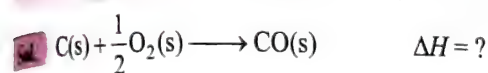
EXAMPLE 6.32

Boiling point of an organic compound is 310 K. Its enthalpy of vaporisation per mole $\Delta_{\text{vap}}H$ is 27.9 kJ mol⁻¹. Calculate the entropy of vaporisation $\Delta_{\text{vap}}S$ of organic compound.

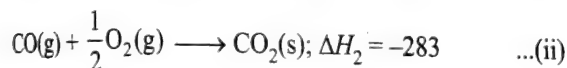
$$\Delta S = \frac{\Delta_{\text{vap}}H}{T} = \frac{27.9}{310} = 0.09 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

EXAMPLE 6.33

The enthalpies of combustion of carbon and carbon monoxide in excess of oxygen at 298 K and constant pressure are -393.5 and -283.0 kJ mol⁻¹, respectively. Calculate the heat of formation of carbon monoxide at constant volume.



Given:



$$\begin{aligned}
 \Delta_f H &= \Delta H_1 - \Delta H_2 \\
 &= 393.5 - (-283) = -110.5 \text{ kJ}
 \end{aligned}$$

$$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$$

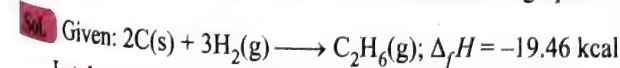
$$\Delta U^\circ = \Delta H - \Delta n_g RT$$

$$= -110.5 - \left(-\frac{1}{2} \right) \times 8.314 \times 10^{-3} \times 298$$

$$= -111.7 \text{ kJ mol}^{-1}$$

EXAMPLE 6.34

The heat of formation of ethane is -19.46 kcal. Bond energies of H-H, C-H, and C-C bonds are 104.18, 99.0, and 80.0 kcal, respectively. Calculate the heat of atomisation of graphite.



Let the heat of atomisation is x kcal

$$\text{BE of reactant} = 2x + 3 \times (\text{H-H})$$

$$= 2x + 3 \times 104.18 = 2x + 312.54$$

$$\text{BE of products} = (\text{C-C}) + 6(\text{C-H})$$

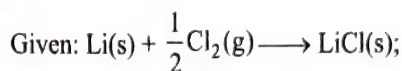
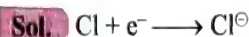
$$= 80 + 6 \times 99 = 674$$

$$\Delta H = 2x + 312.54 - 674 = -19.46$$

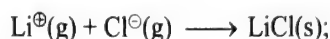
$$\therefore x = 171 \text{ kcal}$$

EXAMPLE 6.35

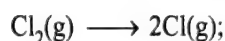
Find the electron affinity of chlorine from the following data. Enthalpy of formation of LiCl is -97.5 kcal mol⁻¹, lattice energy of LiCl = -197.7 kcal mol⁻¹. Dissociation energy of chlorine is 57.6 kcal mol⁻¹, sublimation enthalpy of lithium = +38.3 kcal mol⁻¹, ionisation energy of lithium = 123.8 kcal mol⁻¹.



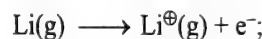
$$\Delta H_1 = -97.5 \text{ kcal mol}^{-1}$$



$$\Delta H_2 = -197.7 \text{ kcal mol}^{-1}$$

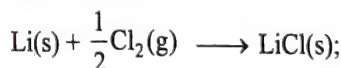


$$\Delta H_3 = 57.6 \text{ kcal mol}^{-1}$$

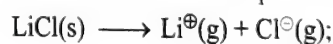


$$\Delta H_5 = 123.8 \text{ kcal mol}^{-1}$$

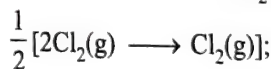
Rewriting equations:



$$\Delta H_1 = -97.5 \text{ kcal mol}^{-1}$$



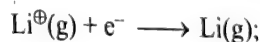
$$\Delta H_2 = -197.7 \text{ kcal mol}^{-1}$$



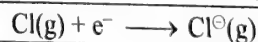
$$\Delta H_3 = \frac{1}{2} \times -57.6 \text{ kcal mol}^{-1}$$



$$\Delta H_4 = -38.3 \text{ kcal mol}^{-1}$$



$$\Delta H_5 = -123.8 \text{ kcal mol}^{-1}$$



$$\begin{aligned}
 \Delta H &= -97.5 + 197.7 - \frac{1}{2} \times 57.6 - 38.3 - 123.8 \\
 &= -90.7 \text{ kcal mol}^{-1}
 \end{aligned}$$

or

Operating:

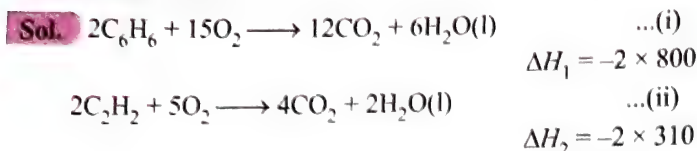
$$\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 - \Delta H_4 - \Delta H_5$$

$$= 97.5 - (-197.7) - \frac{1}{2} (57.6) - 38.3 - 123.8$$

$$= -90.7 \text{ kcal mol}^{-1}$$

EXAMPLE 6.36

The heat of combustion at constant volume at 27°C of benzene and acetylene are -800 kcal and -310 kcal. Find the heat of polymerisation of acetylene to benzene at constant pressure.



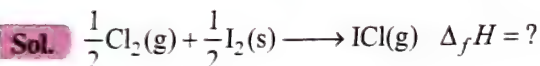
Multiply equation (ii) by 3 and then subtract:

$$\begin{aligned} 6\text{C}_2\text{H}_2 &= 2\text{C}_6\text{H}_6 \\ \Delta H &= 3(-620) - (-1600) = -260 \text{ kcal} \\ 3\text{C}_2\text{H}_2(\text{g}) &= \text{C}_6\text{H}_6(\text{l}) \\ \Delta H &= -\frac{260}{2} = -130 \\ \Delta H &= 0 - 3 = -3 \\ \Delta H &= -130000 - 3 \times 1.987 \times 300 = -131.8 \text{ kcal} \end{aligned}$$

EXAMPLE 6.37

Calculate $\Delta_f H^\ominus \text{ICl(g)}$ from the data

$$\begin{aligned} \Delta H \text{ dissociation } \text{Cl}_2(\text{g}) &= 57.9 \text{ kcal mol}^{-1} \\ \Delta H \text{ dissociation } \text{I}_2(\text{g}) &= 36.1 \text{ kcal mol}^{-1} \\ \Delta H \text{ dissociation } \text{ICl(g)} &= 50.5 \text{ kcal mol}^{-1} \\ \Delta H \text{ sublimation } \text{I}_2(\text{g}) &= 15.0 \text{ kcal mol}^{-1} \end{aligned}$$



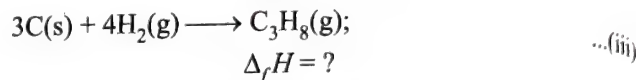
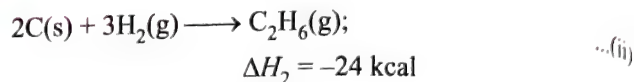
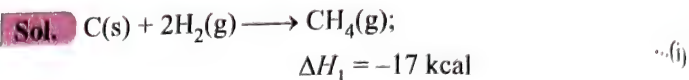
$$\begin{aligned} 1/2 \left\{ \begin{array}{ll} \text{I}_2(\text{g}) \longrightarrow 2\text{I(g)}; & \Delta H_1 = 36.1 \times 1/2 \\ \text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl(g)}; & \Delta H_2 = 57.9 \times 1/2 \\ \text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{g}); & \Delta H_3 = 15.0 \times 1/2 \\ \text{ICl(g)} \longrightarrow \text{I(g)} + \text{Cl(g)}; & \Delta H_4 = 50.5 \end{array} \right. \end{aligned}$$

$$\Delta H = \frac{1}{2}(36.1 + 57.9 + 15.0) - 50.5 = 4 \text{ kcal mol}^{-1}$$

EXAMPLE 6.38

From the following data, calculate the standard enthalpy of formation of propane $\Delta_f H^\ominus \text{CH}_4 = -17 \text{ kcal mol}^{-1}$

$$\Delta_f H^\ominus \text{C}_2\text{H}_6 = -24 \text{ kcal mol}^{-1}; \text{BE(C—H)} = 99 \text{ kcal mol}^{-1} \\ \text{(C—C)} = 84 \text{ kcal mol}^{-1}.$$



From equations (i) and (ii), we get

Let $x \text{ kcal mol}^{-1}$ is the energy of $\text{C(s)} \longrightarrow \text{C(g)}$

Let $y \text{ kcal mol}^{-1}$ is the BE energy of (H—H)

From equation (i), we get

$$-17 = x + 2y - 4 \times 99$$

From equation (ii), we get

$$-24 = 2x + 3y - (84 + 6 \times 99)$$

Solve for x and y ,

$$x = 171 \text{ kcal}, y = 104 \text{ kcal}$$

From equation (iii), we get

$$\begin{aligned} \Delta_f H &= 3x + 4y - [2 \times 84 + 8 \times 99] \\ &= -31 \text{ kcal mol}^{-1} \end{aligned}$$

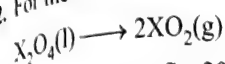
Exercises

Single Correct Answer Type

1. Heat of neutralisation of CsOH with all strong acid is $13.4 \text{ kcal mol}^{-1}$. The heat released on neutralisation of CsOH with HF (weak acid) is $16.4 \text{ kcal mol}^{-1}$. ΔH^\ominus of ionisation of HF is

- (1) 3.0 kcal (2) -3.0 kcal (3) 6.0 kcal (4) 0.3 kcal

2. For the reaction

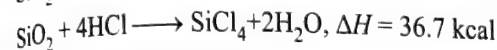
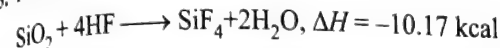


$$\Delta U = 2.1 \text{ kcal}, \Delta S = 20 \text{ cal K}^{-1} \text{ at } 300 \text{ K.}$$

Hence ΔG is

- (1) 2.7 kcal (2) -2.7 kcal (3) 9.3 kcal (4) -9.3 kcal

3. For the given reactions



It may be concluded that

- (1) HF will attack SiO_2 and HCl will not
(2) HCl will attack SiO_2 and HF will not
(3) HF and HCl both attack SiO_2
(4) None attacks SiO_2

4. If $\Delta G = \Delta H - T \Delta S$ and $\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_P$ then variation of EMF of a cell E , with temperature T , is given by:

- (1) $\frac{\Delta H}{nF}$ (2) $\frac{\Delta G}{nF}$ (3) $\frac{\Delta S}{nF}$ (4) $-\frac{\Delta S}{nF}$

5. Which is not intensive property?

- (1) Boiling point (2) Refractive index
(3) Molarity (4) Volume

6. 1 g H_2 gas STP is expanded so that the volume is doubled. Hence, work done is

- (1) 22.4 L-atm (2) 5.6 L-atm
(3) 11.2 L-atm (4) 44.8 L-atm

7. 1 mol of NH_3 gas at 27°C is expanded under adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done, respectively, are

- (1) $150 \text{ K}, 900 \text{ cal}$ (2) $150 \text{ K}, 400 \text{ cal}$
(3) $250 \text{ K}, 1000 \text{ cal}$ (4) $200 \text{ K}, 800 \text{ cal}$

8. Temperature of 1 mol of a gas is increased by 1° at constant pressure. The work done is

- (1) R (2) $2R$ (3) $R/2$ (4) $3R$

9. The standard heat of combustion of Al is $-837.8 \text{ kJ mol}^{-1}$ at 25°C . If Al reacts with O_2 at 25°C , which of the following release 250 kJ of heat?

- (1) The reaction of 0.624 mol of Al

(2) The formation of 0.624 mol of Al_2O_3

(3) The reaction of 0.312 mol of Al

(4) The formation of 0.150 mol of Al_2O_3

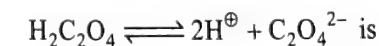
10. $C_p - C_v = R$. This R is

- (1) Change in KE.
(2) Change in rotational energy.
(3) Work done which system can do on expanding the gas per mol per degree increase in temperature.
(4) All correct.

11. Carnot's cycle is said to have 25% efficiency when it operates between T (source) and 300 K (sink). Temperature T is

- (1) 300 K (2) 350 K (3) 375 K (4) 400 K

12. The heat of neutralisation of oxalic acid is $-25.4 \text{ kcal mol}^{-1}$ using strong base, NaOH. Hence, the enthalpy change of the process is



- (1) 2.0 kcal (2) -11.8 kcal
(3) 1.0 kcal (4) -1.0 kcal

13. If a gas absorbs 200 J of heat and expands by 500 cm^3 against a constant pressure of $2 \times 10^5 \text{ N m}^{-2}$, then the change in internal energy is

- (1) -300 J (2) -100 J (3) $+100 \text{ J}$ (4) $+300 \text{ J}$

14. Inversion temperature is

- (1) $\frac{Rb}{2a}$ (2) $\frac{2a}{Rb}$ (3) $\frac{Rb}{a}$ (4) $\frac{a}{Rb}$

15. For an ideal gas Joule-Thomson coefficient is:

- (1) Positive
(2) Negative
(3) Zero
(4) Dependent on molecular weight

16. $\Delta_f H(\text{H}_2\text{O}) = -68 \text{ kcal mol}^{-1}$ and ΔH of neutralisation is $-13.7 \text{ kcal mol}^{-1}$, then the heat of formation of OH^\ominus is

- (1) $-68 \text{ kcal mol}^{-1}$ (2) $-54.3 \text{ kcal mol}^{-1}$
(3) $54.3 \text{ kcal mol}^{-1}$ (4) $-71.7 \text{ kcal mol}^{-1}$

17. The heat of hydrogenation of ethene is x_1 and that of benzene is x_2

Hence resonance energy of benzene is

- (1) $x_1 - x_2$ (2) $x_1 + x_2$ (3) $3x_1 - x_2$ (4) $x_1 - 3x_2$

18. $\text{A}(\text{l}) \xrightleftharpoons{1 \text{ atm}} \text{A}(\text{g}), \Delta_{\text{vap}} H = 460.6 \text{ cal mol}^{-1}$,

boiling point = 50 K . What is the boiling point at 10 atm

- (1) 150 K (2) 75 K
(3) 100 K (4) None is correct

19. $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$

- BE ($\text{H}-\text{H}$) = x_1 ; BE ($\text{O}=\text{O}$) = x_2
BE ($\text{O}-\text{H}$) = x_3

Latent heat of vaporisation of water liquid into water vapour = x_4 , then $\Delta_f H$ (heat of formation of liquid water) is

$$(1) x_1 + \frac{x_2}{2} - x_3 + x_4 \quad (2) 2x_3 - x_1 - \frac{x_2}{2} - x_4$$

$$(3) x_1 + \frac{x_2}{2} - 2x_3 - x_4 \quad (4) x_1 + \frac{x_2}{2} - 2x_3 + x_4$$

20. If a certain mass of gas is made to undergo separately adiabatic and isothermal expansions to the same pressure, starting from the same initial conditions of temperature and pressure, then, as compared to that of isothermal expansion, in the case of adiabatic expansion, the final

- (1) Volume and temperature will be higher.
- (2) Volume and temperature will be lower.
- (3) Temperature will be lower but the final volume will be higher.
- (4) Volume will be lower but the final temperature will be higher.

21. The dissolution of NH_4Cl in water is endothermic even though NH_4Cl dissolves in water spontaneously. Which one of the following best explains this behaviour?

- (1) The bonds in solid NH_4Cl are weak
- (2) The entropy-driving force causes dissolution.
- (3) Endothermic processes are energetically favourable
- (4) The dissolving process is unrelated to energy.

22. The enthalpy of formation of hypothetical MgCl is -125 kJ mol^{-1} and for MgCl_2 is -642 kJ mol^{-1} . What is the enthalpy of the disproportionation of MgCl .

- (1) 392 kJ mol^{-1} (2) -392 kJ mol^{-1}
- (3) -767 kJ mol^{-1} (4) -517 kJ mol^{-1}

23. The products of combustion of an aliphatic thiol (RSH) at 298 K are

- (1) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{SO}_2(\text{g})$
- (2) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and $\text{SO}_2(\text{g})$
- (3) $\text{CO}_2(\text{l})$, $\text{H}_2\text{O}(\text{l})$, and $\text{SO}_2(\text{g})$
- (4) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and $\text{SO}_2(\text{l})$

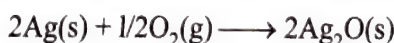
24. Which of the following equations corresponds to the definition of enthalpy of formation at 298 K?

- (1) $\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{l}) \longrightarrow \text{CH}_3\text{OH}(\text{g})$
- (2) $\text{C}(\text{diamond}) + 2\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l})$
- (3) $2\text{C}(\text{graphite}) + 4\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CH}_3\text{OH}(\text{l})$
- (4) $\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l})$

25. Which of the following equations corresponds to the enthalpy of combustion at 298 K?

- (1) $\text{C}_2\text{H}_6(\text{g}) + 7/2\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
- (2) $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- (3) $\text{C}_2\text{H}_6(\text{g}) + 7/2\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$
- (4) $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

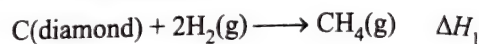
26. For the combustion reaction at 298 K



Which of the following alternatives is correct?

- (1) $\Delta H = \Delta U$
- (2) $\Delta H > \Delta U$
- (3) $\Delta H < \Delta U$
- (4) ΔH and ΔU bear no relation with each other

27. For the equations



Predict whether

- (1) $\Delta H_1 = \Delta H_2$
- (2) $\Delta H_1 > \Delta H_2$
- (3) $\Delta H_1 < \Delta H_2$
- (4) $\Delta H_1 = \Delta H_2 + \Delta_{\text{vap}} H(\text{C}) + \Delta_{\text{diss}} H(\text{H}_2)$

28. The expression $\Delta_{\text{subl}} H^\ominus = \Delta_{\text{fus}} H^\ominus + \Delta_{\text{vap}} H^\ominus$ is true at all

- (1) Temperatures
- (2) Pressures
- (3) Temperatures and pressures
- (4) Temperatures and 1 atm pressure conditions

29. The word 'standard' in standard molar enthalpy change implies

- (1) Temperature 298 K
- (2) Pressure 1 atm
- (3) Temperature 298 K and pressure 1 atm
- (4) All temperatures and all pressures

30. For which of the following equations, will ΔH be equal to ΔU ?

- (1) $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$
- (2) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$
- (3) $2\text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$
- (4) $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{N}_2\text{O}_5(\text{g})$

31. Enthalpy of the system is given as

- (1) $H + PV$ (2) $U + PV$ (3) $U - PV$ (4) $H - PV$

32. Enthalpy change of a reaction will be equal to

- (1) $\Delta U + P\Delta V$ (2) $\Delta U + V\Delta P$
- (3) $\Delta U + \Delta(PV)$ (4) $\Delta U + (\Delta n_g)\Delta(PV)$

33. The molar enthalpies of combustion of $\text{C}_2\text{H}_2(\text{g})$, $\text{C}(\text{graphite})$ and $\text{H}_2(\text{g})$ are -1300 , -394 , and -286 kJ mol^{-1} , respectively. The standard enthalpy of formation of $\text{C}_2\text{H}_2(\text{g})$ is

- (1) -226 kJ mol^{-1} (2) -626 kJ mol^{-1}
- (3) 226 kJ mol^{-1} (4) 626 kJ mol^{-1}

34. The relationship between enthalpy and internal energy change is

- (1) $\Delta U = \Delta H + P\Delta V$ (2) $\Delta H = \Delta U + P\Delta V$
- (3) $\Delta H = \Delta U - P\Delta V$ (4) $P\Delta V = \Delta U + \Delta H$

35. When a reaction is carried out in a closed vessel

- (1) $q_P < q_V$ (2) $q_P > q_V$ (3) $q_P = q_V$ (4) $q_V = 0$

36. The relationship between the free energy change (ΔG) and entropy change (ΔS) at constant temperature (T) is

- (1) $\Delta G = \Delta H + T\Delta S$ (2) $\Delta H = \Delta G + T\Delta S$
 (3) $T\Delta S = \Delta G + \Delta H$ (4) $\Delta G = -\Delta H - T\Delta S$

37. For the gaseous reaction involving the complete combustion of isobutane

- (1) $\Delta H = \Delta U$ (2) $\Delta H > \Delta U$
 (3) $\Delta H = \Delta U = 0$ (4) $\Delta H < \Delta U$

38. Entropy of system depends upon

- (1) Volume only
 (2) Temperature only
 (3) Pressure only
 (4) Pressure, volume, and temperature

39. For the gaseous reaction: $N_2O_4 \longrightarrow 2NO_2$

- (1) $\Delta H > \Delta U$ (2) $\Delta H < \Delta U$
 (3) $\Delta H = \Delta U$ (4) $\Delta H = 0$

40. For the reversible process, the value of ΔS is given by the expression

- (1) $\Delta H/\Delta T$ (2) $T/q(\text{rev})$
 (3) $q(\text{rev}) \times T$ (4) $q(\text{rev})/T$

41. For a process $H_2O(s) \longrightarrow H_2O(l)$ at 273 K

- (1) $G(\text{ice}) = G(\text{water}) = 0$ (2) $G(\text{ice}) = G(\text{water}) \neq 0$
 (3) $G(\text{ice}) > G(\text{water})$ (4) $G(\text{ice}) < G(\text{water})$

42. Which law of thermodynamic, introduces the concept of entropy

- (1) First law (2) Zeroth law
 (3) Third law (4) Second law

43. In which of the following process ΔH and ΔU are of same magnitude

- (1) Evaporation of $CCl_4(l)$
 (2) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
 (3) $NH_4Cl(s) \longrightarrow NH_4Cl(g)$
 (4) $2HI(g) \longrightarrow H_2(g) + I_2(g)$

44. Energy can transfer from system to surroundings as work if

- (1) There is thermal equilibrium between system and surrounding.
 (2) There is mechanical equilibrium between system and surrounding.
 (3) If pressure of system > atmospheric pressure.
 (4) None of these.

45. At equilibrium state

- (1) $\Delta_{\text{total}} S > 0$ (2) $\Delta_{\text{total}} S < 0$
 (3) $\Delta_{\text{total}} S = 0$ (4) Unpredictable

46. For hypothetical reversible reaction

$1/2A_2(g) + 3/2B_2(g) \longrightarrow AB_3(g)$; $\Delta H = -20 \text{ kJ}$ if standard entropies of A_2 , B_2 , and AB_3 are 60, 40, and $50 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The above reaction will be equilibrium at

- (1) 400 K (2) 500 K (3) 250 K (4) 200 K

47. If $\Delta_f H^\ominus$ of $ICl(g)$, $Cl(g)$, and $I(g)$ is 17.57, 121.34, and $106.96 \text{ J mol}^{-1}$, respectively. Then bond dissociation energy of I-Cl bond is

- (1) 35.15 J mol^{-1} (2) $106.69 \text{ J mol}^{-1}$
 (3) $210.73 \text{ J mol}^{-1}$ (4) 420.9 J mol^{-1}

48. If $S + O_2 \longrightarrow SO_2$; $\Delta H = -298.2 \text{ kJ}$

$SO_2 + 1/2 O_2 \longrightarrow SO_3$; $\Delta H = -98.7 \text{ kJ}$

$SO_3 + H_2O \longrightarrow H_2SO_4$; $\Delta H = -130.2 \text{ kJ}$

$H_2 + 1/2 O_2 \longrightarrow H_2O$; $\Delta H = -287.3 \text{ kJ}$

Then the enthalpy of formation of H_2SO_4 at 298 K is

- (1) -814.4 kJ (2) -650.3 kJ
 (3) -320.5 kJ (4) -233.5 kJ

49. Under which of the following condition is the relation $\Delta H = \Delta U + P \Delta V$ valid for a closed system at

- (1) Constant pressure
 (2) Constant temperature
 (3) Constant temperature and pressure
 (4) Constant temperature, pressure, and composition

50. Evaporation of water is

- (1) An exothermic change
 (2) An endothermic change
 (3) A process where no heat changes occur
 (4) A process accompanied by chemical reaction.

51. Which of the following reaction is endothermic?

- (1) $CaCO_3 \longrightarrow CaO + CO_2$
 (2) $Fe + S \longrightarrow FeS$
 (3) $NaOH + HCl \longrightarrow NaCl + H_2O$
 (4) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

52. Which of the following is an endothermic reaction?

- (1) $2H_2 + O_2 \longrightarrow 2H_2O$
 (2) $N_2 + O_2 \longrightarrow 2NO$
 (3) $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$
 (4) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

53. $H_2 + 1/2 O_2 \longrightarrow H_2O$; $\Delta H^\ominus = -68 \text{ kcal}$

$K + H_2O + aq \longrightarrow KOH(aq) + 1/2 H_2$; $\Delta H^\ominus = -48 \text{ kcal}$

$KOH + aq \longrightarrow KOH(aq)$; $\Delta H^\ominus = -14 \text{ kcal}$

From the above data, the standard heat of formation of KOH in kcal is

- (1) $-68 + 48 - 14$ (2) $-68 - 48 + 14$
 (3) $68 - 48 + 14$ (4) $68 + 48 + 14$

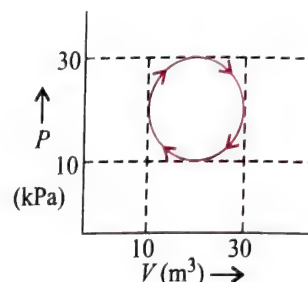
54. Since the enthalpy of elements in their natural state is taken to be zero, the heat of formation ($\Delta_f H$) of compounds

- (1) Is always negative
 (2) Is always positive
 (3) May be negative or positive
 (4) Is zero

55. A reaction, $A + B \longrightarrow C + D + q$, is found to have a positive entropy change, the reaction will be:

- (1) Possible at high temperature
 (2) Possible only at low temperature
 (3) Not possible at any temperature
 (4) Possible at any temperature

56. Molar heat capacity of water in equilibrium with ice at constant pressure is
 (1) Zero (2) Infinity (∞)
 (3) $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (4) $75.48 \text{ J K}^{-1} \text{ mol}^{-1}$
57. Standard molar enthalpy of formation of CO_2 is equal to
 (1) Zero.
 (2) The standard molar enthalpy of combustion of gaseous carbon.
 (3) The sum of standard molar enthalpies of formation of CO and O_2 .
 (4) The standard molar enthalpy of combustion of carbon (graphite).
58. In thermodynamics, a process is called reversible when
 (1) The surroundings and system change into each other.
 (2) There is no boundary between the system and surroundings.
 (3) The surroundings are always in equilibrium with the system.
 (4) The system changes into the surroundings spontaneously.
59. Which one of the following statements is false?
 (1) Work is a state function.
 (2) Temperature is a state function.
 (3) Change in the state is completely defined when the initial and final states are specified.
 (4) Work appears at the boundary of the system.
60. Identify the intensive quantities from the following.
 (1) Enthalpy (2) Temperature
 (3) Volume (4) Refractive index
61. The products of combustion of an aliphatic thiol (RSH) at 298 K are
 (1) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{SO}_2(\text{g})$
 (2) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and $\text{SO}_2(\text{g})$
 (3) $\text{CO}_2(\text{l})$, $\text{H}_2\text{O}(\text{l})$, and $\text{SO}_2(\text{g})$
 (4) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and $\text{SO}_2(\text{l})$
62. For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ mol^{-1} , the minimum value for the energy of activation will be
 (1) Less than ΔH (2) Zero
 (3) More than ΔH (4) Equal to ΔH
- (4) At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
2. Which of the following are intensive properties?
 (1) Heat capacity (2) Refractive index
 (3) Specific volume (4) Entropy
3. Which of the following are extensive properties?
 (1) Elevation in boiling point
 (2) Boiling point
 (3) emf of cell
 (4) E^\ominus of cell
4. Which one is not correct for a cyclic process as shown in the figure?



- (1) $dU = 0$ (2) $q = -w$ (3) 314 J (4) 31.4 J
5. If w_1 , w_2 , w_3 , and w_4 are work done in isothermal, adiabatic, isobaric, and isochoric reversible expansion for an ideal gas, respectively, then
 (1) $w_3 > w_1$ (2) $w_1 > w_2$ (3) $w_2 > w_4$ (4) $w_4 > w_2$
6. Average value of poisson's ratio for a mixture of 2 mol of each gas A and B is 1.66, then
 (1) Gases are mono-atomic
 (2) Gases are diatomic
 (3) Average molar heat capacity at constant volume is 4 cal
 (4) Average molar heat capacity at constant V is 3 cal
7. A reaction attains equilibrium state under standard conditions, then:
 (1) Equilibrium constant $K = 0$
 (2) Equilibrium constant $K = 1$
 (3) $\Delta G^\ominus = 0$ and $\Delta H^\ominus = T \Delta S^\ominus$
 (4) $\Delta G = 0$ and $\Delta H = T \Delta S$
8. The poisson's ratio for O_2 is 1.4. Which of the following are correct for O_2 ?
 (1) $C_{VM} = 5 \text{ cal}$ (2) $C_V = 0.156 \text{ cal}$
 (3) $C_P = \frac{R\gamma}{\gamma - 1}$ (4) $C_V = \frac{R}{(\gamma - 1)}$
9. Select the correct statements.
 (1) The magnitude of work involved in an intermediate irreversible expansion is less than that involved in reversible expansion.
 (2) Heat absorbed during intermediate reversible expansion is more than that in intermediate reversible expansion.
 (3) The magnitude of work involved in an intermediate reversible compression is more than that involved in intermediate irreversible compression.

Multiple Correct Answers Type

1. Select the correct statement

- (1) There is a natural asymmetry between converting work to heat and converting heat to work.
 (2) No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.
 (3) For every chemical reaction at equilibrium, standard change in Gibbs free energy is zero.

- (4) Heat released during intermediate irreversible compression is more than that in intermediate reversible compression.
10. Select the correct statements for the equilibrium under standard conditions.
- $$\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)}; \Delta S^\circ_1$$
- $$\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(v)}; \Delta S^\circ_2$$
- $$\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(v)}; \Delta S^\circ_3$$
- (1) $\Delta S^\circ_1 > \Delta S^\circ_2$ (2) $\Delta S^\circ_2 \gg \Delta S^\circ_1$
 (3) $\Delta S^\circ_3 > \Delta S^\circ_2$ (4) $\Delta S^\circ_3 > \Delta S^\circ_1$
11. Which is intensive property?
- (1) Mass (2) Mass/volume
 (3) Volume (4) Volume/mass
12. Which is an irreversible process?
- (1) Mixing of two gases by diffusion
 (2) Evaporation of water at 373 K and 1 atm pressure
 (3) Dissolution of NaCl in water
 (4) All of the above
13. Which of the following statements are correct?
- (1) Absolute value of enthalpy cannot be determined.
 (2) Absolute value of internal energy cannot be determined.
 (3) Absolute value of entropy can be determined.
 (4) Internal energy, enthalpy, and entropy are intensive properties.
14. Following enthalpy changes are given:
- $\alpha\text{-D glucose(s)} \longrightarrow \alpha\text{-D glucose(aq)}; \Delta H = 10.72 \text{ kJ}$
 $\beta\text{-D glucose(s)} \longrightarrow \beta\text{-D glucose(aq)}; \Delta H = 4.68 \text{ kJ}$
 $\alpha\text{-D glucose(s)} \longrightarrow \beta\text{-D glucose(aq)}; \Delta H = 1.16 \text{ kJ}$
- Calculate enthalpy change in
 $\alpha\text{-D glucose(s)} \longrightarrow \beta\text{-D glucose(s)}$
- (1) 14.24 kJ (2) 16.56 kJ (3) -7.2 kJ (4) 4.88 kJ
15. If x and y are arbitrary extensive variables, then
- (1) $(x + y)$ is an extensive variable.
 (2) x/y is an intensive variable.
 (3) dx/dy is an intensive variable.
 (4) Both (2) and (3).
16. If x and y are arbitrary intensive variables, then
- (1) xy is an intensive variable.
 (2) x/y is an intensive variable.
 (3) $(x + y)$ is an extensive property.
 (4) dx/dy is an intensive property.
17. For which process does $\Delta U = 0$ holds true?
- (1) Cyclic process (2) Isothermal expansion
 (3) Isochoric process (4) Adiabatic process
18. Which is correct about ΔG° ?
- (1) $\Delta G = \Delta H - T \Delta G$
 (2) At equilibrium, $\Delta G^\circ = 0$
 (3) At equilibrium $\Delta G = -RT \log K$
 (4) $\Delta G = \Delta G^\circ + RT \log K$
19. Which is not correct relationship between ΔG° and equilibrium constant K_p .
- (1) $K_p = -RT \log \Delta G^\circ$ (2) $K_p = [e/RT]^{\Delta G^\circ}$
 (3) $K_p = -\frac{\Delta G^\circ}{RT}$ (4) $K_p = e^{-\Delta G^\circ/RT}$
20. Which is not correct relationship?
- (1) $\left[\frac{dH}{dT} \right]_P - \left[\frac{dU}{dT} \right]_T = (+ve)$
 (2) $\left[\frac{dU}{dV} \right]_T = 0$ (for ideal gas)
 (3) $\left[\frac{dV}{dT} \right]_P = \frac{nR}{P}$ (for ideal gas)
 (4) All of these
21. Which of the following are endothermic processes?
- (1) Combustion of glucose
 (2) Decomposition of water
 (3) Dehydrogenation of ethane to ethene
 (4) Conversion of graphite to diamond
22. For an ideal gas undergoing isothermal irreversible expansion
- (1) $\Delta U = 0$ (2) $\Delta H = 0$ (3) $\Delta S = 0$ (4) $w = 0$
23. In which of the following reactions, $\Delta H > \Delta U$?
- (1) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$
 (2) $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (3) $2\text{H}_2\text{O}_2(\text{l}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
 (4) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
24. Which of the following are not correct at 298 K?
- (1) $\Delta_f G^\circ \text{ element} = 0$ (2) $\Delta_f H^\circ \text{ element} = 0$
 (3) $\Delta_f S^\circ \text{ element} = 0$ (4) $\Delta_f G^\circ \text{ compound} = 0$
25. Under which of the conditions the process will be spontaneous?
- (1) $\Delta G = -ve$ (2) $\Delta_{\text{Total}} S = +ve$
 (3) $\Delta_{\text{Total}} S = -ve$ (4) $\Delta_{\text{Total}} S = 0$
26. The correct expressions for an adiabatic process are
- (1) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$ (2) $\frac{P_2}{P_1} = \left(\frac{T_1}{T_2} \right)^{\frac{\gamma-1}{\gamma}}$
 (3) $P_1 V_1^\gamma = P_2 V_2^\gamma$ (4) $P_1 V_1^{\gamma-1} = P_2 V_2^{\gamma-1}$
27. During an adiabatic reversible expansion of an ideal gas
- (1) Internal energy of the system decreases.
 (2) Temperature of the system decreases.
 (3) The value of γ changes.
 (4) Pressure increases.
28. The intensive property/properties is/are
- (1) Temperature (2) Pressure
 (3) Internal energy (4) Heat capacity
29. The second law of thermodynamics states that
- (1) All spontaneous processes are thermodynamically irreversible.
 (2) Entropy of the universe is continuously increasing.

- (3) Energy can neither be created nor destroyed.
 (4) Energy of the universe remain constant.
30. The criteria for spontaneity of a process is/are
 (1) $(dG)_{TP} < 0$ (2) $(dE)_{SV} < 0$
 (3) $(dH)_{SP} < 0$ (4) $(dS)_{EV} < 0$
31. The following is(are) endothermic reaction(s)
 (1) Combustion of methane
 (2) Decomposition of water
 (3) Dehydrogenation of ethane to ethylene
 (4) Conversion of graphite to diamond
32. For the adiabatic expansion of an ideal gas
 (1) $PI^\gamma = \text{constant}$ (2) $TV^{\gamma-1} = \text{constant}$
 (3) $TP^{1-\gamma} = \text{constant}$ (4) None of the above
33. In which of the following entropy increases?
 (1) Rusting of iron
 (2) Melting of ice
 (3) Crystallisation of sugar from solution
 (4) Vaporisation of camphor
34. Which of the following are irreversible processes?
 (1) Mixing of two gases.
 (2) Evaporation of water at 373 K and 1 atm in a closed system.
 (3) Dissolution of NaCl in water.
 (4) $H_2O(s)$ at -4°C
35. Which of the options given below are correct?
- | ΔH | ΔS | Nature of reaction |
|------------|------------|--|
| (1) (-) | (+) (+) | Spontaneous at all temperatures |
| (2) (+) | (-) (-) | Nonspontaneous regardless of temperature |
| (3) (+) | (+) (+) | Spontaneous only at high temperature |
| (4) (-) | (-) (-) | Spontaneous only at low temperature |
36. Which of the following are thermodynamically stable?
 (1) C(diamond) (2) C(graphite)
 (3) $P_4(\text{white})$ (4) $P_4(\text{black})$
37. Which of the following affect the heat of reaction?
 (1) Physical states of reactants and products
 (2) Allotropic forms of elements
 (3) Temperature
 (4) Reaction carried out at constant pressure or constant volume
38. Which of the following type of energies are involved in Born Haber's cycle?
 (1) $\Delta_{\text{sub}}H$
 (2) Ionisation energy
 (3) Bond dissociation energy
 (4) Lattice energy
39. Which of the following are true about resonance energy?
 (1) Resonance energy = Experimental heat of formation - Calculated heat of formation.
 (2) Resonance energy = Calculated heat of formation - Experimental heat of formation.
 (3) Greater the resonance energy, more the compound will be stable.
 (4) Lesser the resonance energy, more the compound will be stable.
40. Hess' law is applicable for determination of enthalpy of
 (1) Reaction (2) Formation
 (3) Transition (4) None of these
41. Indicate in which case/cases the spontaneity of a change is favoured when
 (1) ΔG is +ve (2) ΔH is -ve
 (3) ΔS is +ve (4) ΔS is -ve
 (5) ΔG is -ve
42. Endothermic reactions, having $\Delta S = +ve$ may be spontaneous if
 (1) $\Delta H > T \Delta S$ (2) $\Delta H < T \Delta S$
 (3) $\Delta H = T \Delta S$ (4) T is very high
43. For gaseous reactions, if ΔH is the change in enthalpy and ΔU that in internal energy, then
 (1) ΔH is always greater than ΔU .
 (2) ΔH is always less than ΔU .
 (3) $\Delta H < \Delta U$ only if the number of mole of the products is less than that of the reactants.
 (4) $\Delta U < \Delta H$ only if the number of mole of the reactants is less than that of the products.
44. Which of the following statements is/are incorrect?
 (1) The entropy of the universe decreases and increases at a periodic rate.
 (2) The entropy of the universe increases and tends towards the maximum value.
 (3) For endothermic spontaneous processes the total entropy change decreases.
 (4) The entropy of the universe decreases and tends to zero.
45. The open system(s) is/are which
 (1) Can exchange matter with the surroundings.
 (2) Can exchange energy with the surroundings.
 (3) Can exchange both matter and energy with the surroundings.
 (4) Cannot exchange either matter or energy with the surroundings.
46. In a reaction, ΔH and ΔS both are more than zero. In which of the following cases, the reaction would not be spontaneous?
 (1) $\Delta H > T \Delta S$ (2) $T \Delta S > \Delta H$
 (3) $\Delta H = T \Delta S$ (4) $\Delta G < 0$
47. If W is work done by the system (-ve), the mathematical representation of the first law of thermodynamics is/are
 (1) $\Delta U = \Delta q - W$ (2) $q = \Delta U - W$
 (3) $dq + dW = 0$ (4) $\Delta U = q + W$
48. In which reaction(s), ΔS is negative?
 (1) $H_2O(l) \longrightarrow H_2O(s)$
 (2) $3O_2(g) \longrightarrow 2O_3(g)$
 (3) $H_2O(l) \longrightarrow H_2O(g)$
 (4) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
49. The heat evolved in the combustion of benzene is given by

$$C_6H_6(l) + 7\frac{1}{2}O_2(g) \longrightarrow 3H_2O(l) + 6CO_2(g),$$

$$\Delta H = -781.0 \text{ kcal mol}^{-1}$$

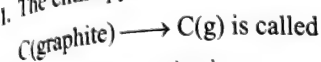
When 156 g of C_6H_6 is burnt in an open container, the amount of heat energy released will be

- (1) 150.2 kcal mol⁻¹ (2) 1562.0 kcal mol⁻¹
 (3) 6528.2 kJ mol⁻¹ (4) 2448.5 kJ mol⁻¹

60. The heat of neutralization of a strong acid by a strong base is a constant

- (1) 57.0 kJ mol⁻¹ (2) 13.7 kcal mol⁻¹
 (3) $5.7 \times 10^4 \text{ J mol}^{-1}$ (4) $13.7 \times 10^3 \text{ cal mol}^{-1}$

61. The enthalpy change for the process



- (1) Heat of vaporisation
 (2) Heat of sublimation
 (3) Heat of allotropic change
 (4) Heat of atomisation

62. Enthalpy change equal internal energy change when

- (1) All the reactants and products are in solution
 (2) Reaction is carried out in a closed vessel
 (3) Number of moles of gaseous reactants and that of products is equal
 (4) Reaction is carried out at constant pressure

Linked Comprehension Type

Paragraph 1

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy changes of the process as

$$(\Delta G)_{PT} = \Delta H - T \Delta S$$

The magnitude of ΔH does not change much with the change in temperature but the entropy factor $T \Delta S$ changes appreciably. Thus, spontaneity of a process depends very much on temperature.

1. When CaCO_3 is heated to a high temperature, it undergoes decomposition into CaO and CO_2 whereas it is quite stable at room temperature. The most likely explanation of it is

- (1) The enthalpy of reaction (ΔH) overweighs the term $T \Delta S$ at high temperature.
 (2) The term $T \Delta S$ overweighs the enthalpy of reaction at high temperature
 (3) At high temperature, both enthalpy of reaction and entropy change become negative.
 (4) None of these.

2. For the reaction at 25°C, $\text{X}_2\text{O}_4(\text{l}) \longrightarrow 2\text{XO}_2$

$\Delta H = 2.0 \text{ kcal}$ and $\Delta S = 20 \text{ cal K}^{-1}$. the reaction would be

- (1) Spontaneous (2) At equilibrium
 (3) Unpredictable (4) Non-spontaneous

3. For the reaction at 298 K, $2\text{A} + \text{B} \rightarrow \text{C}$

$\Delta H = 100 \text{ kcal}$ and $\Delta S = 0.020 \text{ kcal K}^{-1}$. If ΔH and ΔS are assumed to be constant over the temperature range, at what temperature will the reaction become spontaneous?

- (1) 1000 K (2) 3500 K (3) 5000 K (4) 1500 K

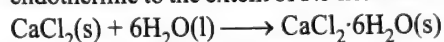
4. A reaction has a value of $\Delta H = -20 \text{ kcal}$ at 200 K, the reaction is spontaneous, below this temperature, it is not. The values ΔG and ΔS at 400 K are, respectively

- (1) 10, -0.1 cal K^{-1} (2) -10 kcal , -100 cal K^{-1}
 (3) 0, 10.0 cal K^{-1} (4) 0, -100 cal K^{-1}

5. The enthalpy change for a certain reaction at 300 K is $-15.0 \text{ kcal mol}^{-1}$. The entropy change under these conditions is $-7.2 \text{ cal K}^{-1} \text{ mol}^{-1}$. The free energy change for the reaction and its spontaneous/nonspontaneous character will be

- (1) $-12.84 \text{ kcal mol}^{-1}$, spontaneous
 (2) $-12.16 \text{ kcal mol}^{-1}$, spontaneous
 (3) $12.84 \text{ kcal mol}^{-1}$, non spontaneous
 (4) $12.0 \text{ kcal mol}^{-1}$, spontaneous

6. The dissolution of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in a large volume of water is endothermic to the extent of $3.5 \text{ kcal mol}^{-1}$. For the reaction,



ΔH is -23.2 kcal . The heat of solution of anhydrous CaCl_2 in large quantity of water will be

- (1) $-16.7 \text{ kcal mol}^{-1}$ (2) $-19.7 \text{ kcal mol}^{-1}$
 (3) $19.7 \text{ kcal mol}^{-1}$ (4) $16.7 \text{ kcal mol}^{-1}$

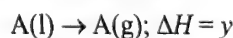
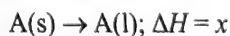
Paragraph 2

The enthalpy change for chemical reaction is denoted as ΔH^\ominus and $\Delta H^\ominus = H_P^\ominus - H_R^\ominus$. The relation between enthalpy and internal energy is expressed by equation:

$$\Delta H = \Delta U + \Delta nRT$$

where ΔU = change in internal energy, Δn = change in number of moles, R = gas constant.

7. Given that:



The heat of sublimation of A will be

- (1) $x - y$ (2) $x + y$ (3) x or y (4) $-(x + y)$

8. $\text{H}_2(\text{g}) + \left(\frac{1}{2}\right)\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l}); \Delta H_{298 \text{ K}} = -68.00 \text{ kcal}$

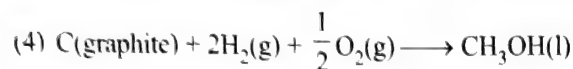
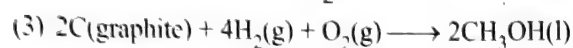
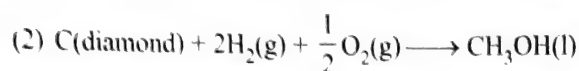
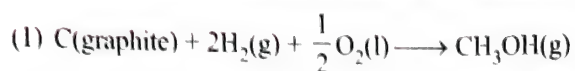
Heat of vaporisation of water at 1 atm and 25°C is 10.00 kcal. The standard heat of formation (in kcal) of a 1 mol vapour at 25°C is

- (1) -78.00 (2) 78.00 (3) +58.00 (4) -58.00

9. For the change, $\text{C}_{\text{diamond}} \longrightarrow \text{C}_{\text{graphite}}; \Delta H = -1.89 \text{ kJ}$, if 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2 the heat liberated in first case is

- (1) Less than in the second case by 1.89 kJ
 (2) Less than in the second case by 11.34 kJ
 (3) Less than in the second case by 14.34 kJ
 (4) More than in the second case by 0.945 kJ

10. Which of the following equations corresponds to the definition of enthalpy of formation at 298 K?



11. Enthalpy of the system is given as

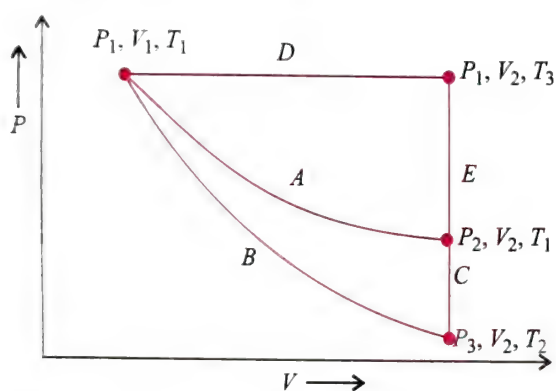
$$(1) H = PV \quad (2) U + PV \quad (3) U - PV \quad (4) H - V$$

12. For a reaction, $2\text{A}(\text{s}) + 2\text{Y}(\text{s}) \longrightarrow 2\text{C}(\text{l}) + \text{D}(\text{g})$, ΔH at 27°C is $-28 \text{ kcal mol}^{-1}$. ΔU is kcal mol^{-1}

$$(1) -25.5 \quad (2) +25.5 \quad (3) -28.6 \quad (4) 28.4$$

Paragraph 3

For an ideal gas, an illustration of three different paths A, (B + C) and (D + E) from an initial state P_1, V_1, T_1 to a final state P_2, V_2, T_1 is shown in the given figure.



Path A represents a reversible isothermal expansion from P_1, V_1 to P_2, V_2 . Path (B + C) represents a reversible adiabatic expansion (B) from P_1, V_1, T_1 to P_3, V_2, T_2 followed by reversible heating the gas at constant volume (C) from P_3, V_2, T_2 to P_2, V_2, T_1 . Path (D + E) represents a reversible expansion at constant pressure P_1 (D) from P_1, V_1, T_1 to P_1, V_2, T_3 followed by a reversible cooling at constant volume V_2 (E) from P_1, V_2, T_3 to P_2, V_2, T_1 .

13. What is q_{rev} for path (A)?

$$(1) P(V_2 - V_1) \quad (2) -nRT_1 \ln \frac{V_2}{V_1}$$

$$(3) -nR \ln \frac{V_2}{V_1} \quad (4) -nRT_1 \ln \frac{V_2}{V_1}$$

14. What is q_{rev} for path (B + C)?

$$(1) nR \ln \frac{V_2}{V_1} \quad (2) -nR \ln \frac{V_2}{V_1}$$

$$(3) \text{zero} \quad (4) nRT_1 \ln \frac{V_2}{V_1}$$

15. What is ΔS for path A?

$$(1) nR \ln \frac{V_2}{V_1} \quad (2) P(V_2 - V_1)$$

$$(3) -P(V_2 - V_1) \quad (4) nR(V_2 - V_1)$$

16. What is q_{rev} for path (D + E)?

$$(1) P(V_2 - V_1)$$

$$(2) \int_{T_1}^{T_3} \frac{C_V(T)}{T} dT$$

$$(3) nR \ln \frac{V_2}{V_1}$$

$$(4) \int_{T_1}^{T_3} C_V(T) dT$$

17. What is ΔS for path (D + E)?

$$(1) -P(V_2 - V_1)$$

$$(2) -nR \ln \frac{V_2}{V_1}$$

$$(3) +P(V_2 - V_1)$$

$$(4) nR \ln \frac{V_2}{V_1}$$

Paragraph 4

Concrete is produced from a mixture of cement, water and small stones. Small amount of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is added in cement production to improve the subsequent hardening of concrete. The elevated temperature during the production of cement may lead to the formation of unwanted hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ according to reaction.



The $\Delta_f H^\ominus$ of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{O}(\text{g})$

are $-2021.0 \text{ kJ mol}^{-1}$, $-1575.0 \text{ kJ mol}^{-1}$, and $-241.8 \text{ kJ mol}^{-1}$, respectively. The respective values of their standard entropies are $194.0, 130.0$, and $188.0 \text{ J K}^{-1} \text{ mol}^{-1}$. The values of $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0831 \text{ L bar mol}^{-1} \text{ K}^{-1}$.

Answer the following questions on the basis of above information.

18. Heat change occurring during conversion of 1 kg of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ (molar mass 172 g mol^{-1}) of

$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}(\text{s})$ is equal to

$$(1) 484 \text{ kJ mol}^{-1} \quad (2) 400 \text{ kJ}$$

$$(3) -484.0 \text{ kJ mol}^{-1} \quad (4) -1000 \text{ kJ}$$

19. The value of ΔG^\ominus for the reaction at 298 K is

$$(1) 120 \text{ kJ mol}^{-1} \quad (2) 17.92 \text{ kJ mol}^{-1}$$

$$(3) -180 \text{ kJ mol}^{-1} \quad (4) 10 \text{ kJ mol}^{-1}$$

20. The value of equilibrium constant for reaction is

$$(1) \approx 0 \quad (2) < 1 \quad (3) > 1 \quad (4) = 1$$

21. The equilibrium pressure of water vapour in closed vessel

containing $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}(\text{s})$, and $\text{H}_2\text{O}(\text{g})$

at 298 K (Antilog $-3.14 = 7.24 \times 10^{-4}$) is

$$(1) (17.24 \times 10^{-4}) \text{ bar} \quad (2) (-7.24 \times 10^{-4})^3 \text{ bar}$$

$$(3) (18 \times 10^{-4})^{2/3} \text{ bar} \quad (4) (7.24 \times 10^{-4})^{2/3} \text{ bar}$$

22. The formation of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at 298 K is

$$(1) \text{Spontaneous}$$

$$(2) \text{Endothermic and non-spontaneous}$$

$$(3) \text{Endothermic and non-spontaneous}$$

$$(4) \text{Exothermic and non-spontaneous}$$

Paragraph 5

A sample of ideal gas undergoes isothermal expansion in a reversible manner from volume V_1 to volume V_2 . The initial pressure is P_1 and the final pressure is P_2 . The same sample is then allowed to undergo reversible expansion under adiabatic conditions from volume V_1 to V_2 . The initial pressure being same but final pressure is P_2 .

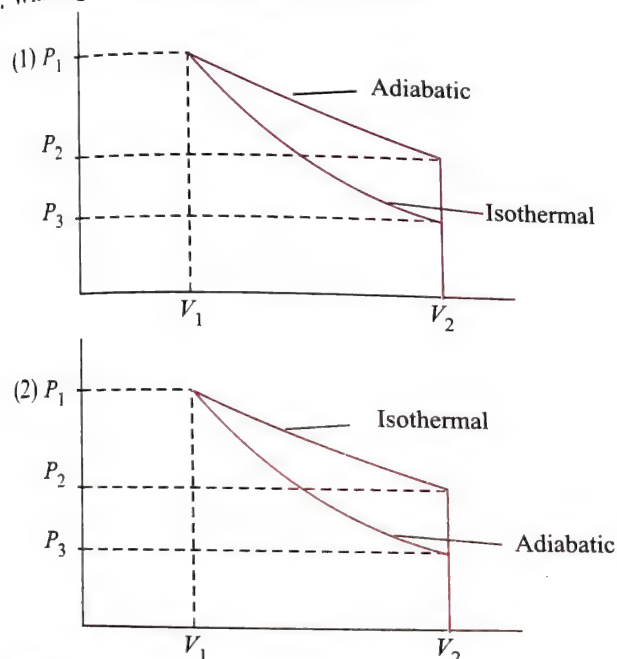
23. The work of expansion in adiabatic process (w_{adi}) is related to work of expansion in isothermal process (w_{iso}) as

- (1) $w_{\text{adi}} = w_{\text{iso}}$ (2) $w_{\text{adi}} < w_{\text{iso}}$
 (3) $w_{\text{adi}} = 2w_{\text{iso}}$ (4) $w_{\text{adi}} > w_{\text{iso}}$

24. Which of the following is correct?

- (1) $P_1 V_1 = P_2 V_2$ (2) $P_1/P_2 = V_1/V_2$
 (3) $P_1/P_2 = P_1/P_3$ (4) $P_1 = P_2$

25. Which graphic representation is correct



- (3) Both (1) and (2) (4) None

26. If P_3 and P_2 are equal, then

- (1) $V_{2(\text{adi})} = V_{2(\text{iso})}$
 (2) $V_{2(\text{adia})} < V_{2(\text{iso})}$
 (3) Both $V_{2(\text{adi})} = V_{2(\text{iso})} < V_1$
 (4) $V_{2(\text{adi})} > V_{2(\text{iso})}$

27. Which relation is correct $\left(\gamma = \frac{C_p}{C_v}\right)$?

- (1) $P_1 V_1 = P_2 V_3$ (2) $P_2 V_1 = P_3 V_2$
 (3) $P_1 V_1^\gamma = P_2 V_2^\gamma$ (4) $\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

Paragraph 6

Free energy, $G = H - TS$, is a state function that indicates whether a reaction is spontaneous or non-spontaneous. If you think of TS as the part of the system's energy that is disordered already, then $(H - TS)$ is the part of the system's energy that is still ordered and therefore free to cause spontaneous change by becoming disordered.

$$\text{Also, } \Delta G = \Delta H - T \Delta S$$

From the second law of thermodynamics, a reaction is spontaneous if $\Delta_{\text{total}} S$ is positive, non-spontaneous if $\Delta_{\text{total}} S$ is negative, and at equilibrium if $\Delta_{\text{total}} S$ is zero.

Since, $-T \Delta S = \Delta G$ and since ΔG and ΔS have opposite signs, we can restate the thermodynamic criterion for the spontaneity of a reaction carried out at a constant temperature and pressure.

If $\Delta G < 0$, the reaction is spontaneous.

If $\Delta G > 0$, the reaction is non-spontaneous.

If $\Delta G = 0$, the reaction is at equilibrium.

Read the above paragraph carefully and answer the following questions based on the above comprehension.

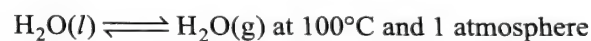
28. For the spontaneity of a reaction, which statement is true?

- (1) $\Delta G = +ve$; $\Delta H = +ve$ (2) $\Delta H = +ve$; $\Delta S = -ve$
 (3) $\Delta G = -ve$; $\Delta S = -ve$ (4) $\Delta H = -ve$; $\Delta S = +ve$

29. A particular reaction has a negative value for the free energy change. Then at ordinary temperature

- (1) It has a large (-ve) value for the entropy change
 (2) It has large (+ve) value for enthalpy change
 (3) It has a small (+ve) value for enthalpy change
 (4) It has a (+ve) value for the entropy change and a (-ve) value for enthalpy change.

30. Which of the following is true for the reaction?



- (1) $\Delta S = 0$ (2) $\Delta U = \Delta H$ (3) $\Delta H = 0$ (4) $\Delta H = T \Delta S$

31. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then

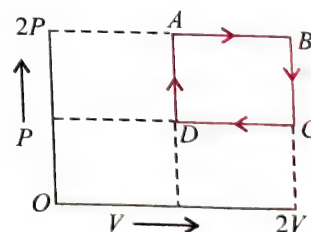
- (1) ΔH is (-ve) and ΔS is (+ve).
 (2) ΔH and ΔS both are (+ve).
 (3) ΔH and ΔS both are (-ve).
 (4) ΔH is (+ve) and ΔS is (-ve).

32. One mol of ice is converted to liquid at 273 K; $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$ have entropies 38.20 and 60.03 $\text{J mol}^{-1} \text{ dg}^{-1}$. Enthalpy change in the conversion will be

- (1) 59.59 J mol^{-1} (2) 593.95 J mol^{-1}
 (3) 5959.5 J mol^{-1} (4) 59595 J mol^{-1}

Paragraph 7

The state of a mole of an ideal gas changed from state A at pressure $2P$ and volume V follows four different processes and finally returns to initial state A reversibly as shown below in the graph. By interpreting the graph, answer the following questions.



33. Which is the kind of process followed from state A to state B?

- (1) Isochoric expansion
 (2) Isobaric expansion
 (3) Isothermal reversible expansion
 (4) Isothermal irreversible compression

34. In state D to state A , what kind of process is followed?

- (1) Isobaric expansion (2) Isobaric compression
(3) Isochoric process (4) Isothermal compression

35. What would be the total work done by the gas?

- (1) $-PV$ (2) PV
(3) 0 (4) None of these

36. What would be the work done in state B to C ?

- (1) $-PV$ (2) PV (3) $2PV$ (4) Zero

37. What would be the heat absorbed by the system in this cyclic process?

- (1) $-2PV$ (2) Zero (3) $2PV$ (4) PV

Paragraph 8

The second law of thermodynamics is a fundamental law of science. In this problem, we consider the thermodynamics of an ideal gas, phase transition, and chemical equilibrium.

Three moles of CO_2 gas expands isothermally (in thermal contact with the surroundings; temperature = 15.0°C) against a fixed external pressure of 1.00 bar. The initial and final volumes of the gas are 10.0 L and 30.0 L, respectively.

38. Select the correct order of the entropy change.

- (1) $\Delta_{\text{sys}}S > 0$, $\Delta_{\text{surr}}S = 0$ (2) $\Delta_{\text{sys}}S < 0$, $\Delta_{\text{surr}}S > 0$
(3) $\Delta_{\text{sys}}S > 0$, $\Delta_{\text{surr}}S < 0$ (4) $\Delta_{\text{sys}}S > 0$, $\Delta_{\text{surr}}S = 0$

39. Assuming CO_2 to be an ideal gas, $\Delta_{\text{sys}}S$ is

- (1) 27.4 J K^{-1} (2) 9.1 J K^{-1}
(3) -27.4 J K^{-1} (4) -9.1 J K^{-1}

40. $\Delta_{\text{surr}}S$ is

- (1) 27.4 J K^{-1} (2) $+6.94 \text{ J K}^{-1}$
(3) 0.00 J K^{-1} (4) -6.94 J K^{-1}

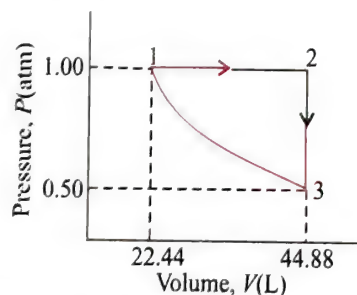
41. Change in entropy of the universe is

- (1) 34.34 J K^{-1} (2) -34.34 J K^{-1}
(3) 20.46 J K^{-1} (4) -20.46 J K^{-1}

Paragraph 9

A sample consisting of 1 mol of a mono-atomic perfect gas

($C_V = \frac{3}{2}R$) is taken through the cycle as shown.



42. Temperature at points (1), (2), and (3), respectively is

- (1) 273 K, 546 K, 273 K (2) 546 K, 273 K, 273 K
(3) 273 K, 273 K, 273 K (4) 546 K, 546 K, 273 K

43. ΔH for the overall cycle is

- (1) $+5.67 \times 10^3 \text{ J}$ (2) $-5.67 \times 10^3 \text{ J}$
(3) $-11.34 \times 10^3 \text{ J}$ (4) Zero

44. ΔU for the process (1 \rightarrow 2) is

- (1) 0.00 J (2) $+3.40 \times 10^3 \text{ kJ}$
(3) -3.40 J (4) $-3.40 \times 10^3 \text{ J}$

45. ΔU for the process (2 \rightarrow 3) is

- (1) 0.00 J (2) $+3.40 \text{ kJ}$
(3) -3.40 kJ (4) None of these

Paragraph 10

Chemical reactions are invariably associated with the transfer of energy either in the form of heat or light. In the laboratory, heat changes in physical and chemical processes are measured with an instrument called calorimeter. Heat change in the process is calculate as

$$q = ms \Delta T \quad s = \text{Specific heat}$$

$$= c\Delta T \quad c = \text{Heat capacity}$$

Heat of reaction at constant volume is measured using bomb calorimeter.

$$q_V = \Delta U = \text{Internal energy change}$$

Heat of reaction at constant pressure is measured using simple or water calorimeter.

$$q_P = \Delta H$$

$$q_P = q_V + P \Delta V$$

$$\Delta H = \Delta U + \Delta nRT$$

46. Match List I with List II and select the answer from the given codes

List I

- A. $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
B. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
C. $\text{NH}_4\text{HS(s)} \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$
D. $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
E. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

List II

1. $\Delta H = \Delta U + RT$
2. $\Delta H = \Delta U$
3. $\Delta H = \Delta U - 2RT$
4. $\Delta H = \Delta U + 2RT$
5. $\Delta H = \Delta U - RT$

Codes	A	B	C	D	E
(1)	1	2	3	4	5
(2)	5	2	3	4	1
(3)	1	3	4	2	5
(4)	2	3	4	1	5

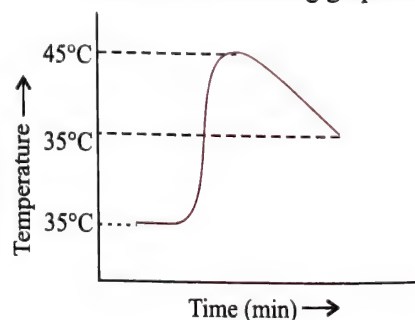
47. The heat capacity of a bomb calorimeter is 500 J K^{-1} . When 0.1 g of methane was burnt in this calorimeter, the temperature rose by 2°C . The value of ΔU per mole will be

- (1) $+2 \text{ kJ}$ (2) -2 kJ (3) $+260 \text{ kJ}$ (4) -160 kJ

48. For which reaction will $\Delta H = \Delta U$? Assume each reaction is carried out in an open container

- (1) $4\text{CO(g)} + 2\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g})$
(2) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr(g)}$
(3) $\text{C(s)} + 2\text{H}_2\text{O(g)} \longrightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
(4) $2\text{PCl}_5(\text{g}) \longrightarrow 2\text{PCl}_3(\text{g}) + 2\text{Cl}_2(\text{g})$

49. What value of ΔT should be used for the calorimetry experiment that gives the following graphical results?



(1) 30°C

(2) 45°C

(3) 20°C

(4) 35°C

50. The enthalpy of fusion of ice is 6.02 kJ mol^{-1} . The heat capacity of water is $4.18 \text{ J g}^{-1} \text{ C}^{-1}$. What is the smallest number of ice cubes at 0°C , each containing one mole of water, that are needed to cool 500 g of liquid water from 20°C to 0°C ?

(1) 8

(2) 7

(3) 140

(4) 120

Paragraph 11

Bond energies can be obtained by using the following relation:

$$\Delta H_{\text{reaction}} = \Sigma \text{Bond energy of bonds, broken in the reactants} - \Sigma \text{Bond energy of bonds, formed in the products}$$

Bond energy depends on three factors:

- (I) Greater is the bond length, lesser is the bond energy.
- (II) Bond energy increases with the bond multiplicity.
- (III) Bond energy increases with the electronegativity difference between the bonding atoms.

51. Arrange N—H, O—H, and F—H bonds in the decreasing order of bond energy.

(1) F—H > O—H > N—H (2) N—H > O—H > F—H

(3) O—H > N—H > F—H (4) F—H > N—H > O—H

52. Bond energy of different halogen molecules will lie in the sequences

(1) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (2) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ (3) $\text{I}_2 > \text{Cl}_2 > \text{Br}_2 > \text{F}_2$ (4) $\text{Br}_2 > \text{F}_2 > \text{I}_2 > \text{Cl}_2$

53. Which among the following sequences is correct about the bond energy of C—C, C=C, and C≡C bonds?

(1) $\text{C}=\text{C} > \text{C}\equiv\text{C} > \text{C}-\text{C}$ (2) $\text{C}\equiv\text{C} < \text{C}=\text{C} < \text{C}-\text{C}$ (3) $\text{C}\equiv\text{C} > \text{C}=\text{C} > \text{C}-\text{C}$ (4) $\text{C}\equiv\text{C} > \text{C}-\text{C} > \text{C}=\text{C}$

54. In CH_4 molecule, which of the following statements is correct about the C—H bond energy?

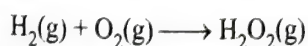
(1) All C—H bonds of methane have same energy.

(2) Average of all C—H bond energies is considered.

(3) Fourth C—H bond requires highest energy to break.

(4) None of the above.

55. Use the bond energies to estimate ΔH for this reaction:



Bond	Bond energy
H—H	436 kJ mol^{-1}
O—O	142 kJ mol^{-1}
O=O	499 kJ mol^{-1}
H—O	460 kJ mol^{-1}

- (1) -127 kJ (2) -109 kJ (3) -400 kJ (4) -800 kJ

56. The heat of formation of NO from its elements is $+90 \text{ kJ mol}^{-1}$. What is the approximate bond dissociation energy of the bond in NO?

$$\text{BE}_{\text{N}=\text{N}} = 941 \text{ kJ mol}^{-1} \quad \text{BE}_{\text{O}=\text{O}} = 499 \text{ kJ mol}^{-1}$$

(1) 630 kJ mol^{-1} (2) 700 kJ mol^{-1} (3) 860 kJ mol^{-1} (4) 810 kJ mol^{-1}

Paragraph 12

A change in the free energy of a system at constant temperature and pressure will be:

$$\Delta_{\text{sys}} G = \Delta_{\text{sys}} H - T \Delta_{\text{sys}} S$$

At constant temperature and pressure

$$\Delta_{\text{sys}} G < 0 \text{ (spontaneous)}$$

$$\Delta_{\text{sys}} G = 0 \text{ (equilibrium)}$$

$$\Delta_{\text{sys}} G > 0 \text{ (non-spontaneous)}$$

57. The free energy for a reaction having $\Delta H = 31400 \text{ cal}$, $\Delta S = 32 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 1000°C is

(1) -9336 cal (2) -7006 cal (3) -2936 cal (4) $+9006 \text{ cal}$

58. For a spontaneous reaction ΔG , equilibrium K and E_{cell}^\ominus will be, respectively

(1) $-\text{ve}, >1, +\text{ve}$ (2) $-\text{ve}, <1, -\text{ve}$ (3) $+\text{ve}, >1, -\text{ve}$ (4) $-\text{ve}, >1, -\text{ve}$

59. For a system in equilibrium, $\Delta G = 0$, under conditions of constant

(1) Temperature and pressure (2) Pressure and volume

(3) Temperature and volume (4) Energy and volume

60. If both ΔH and ΔS are negative, the reaction will be spontaneous

(1) At high temperature

(2) At all temperatures

(3) At low temperature

(4) At high pressure

61. A reaction has positive values of ΔH and ΔS . From this you can deduce that the reaction

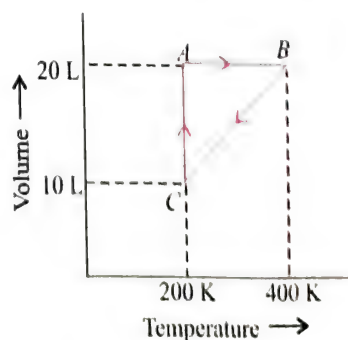
(1) Must be spontaneous at any temperature

(2) Cannot be spontaneous at any temperature

(3) Will be spontaneous only at low temperature

(4) Will be spontaneous only at high temperature

Paragraph 13



Graph for one mole gas

62. Process $A \rightarrow B$ represents

- (1) Isobaric (2) Isochoric
(3) Isothermal (4) Isoentropic

63. The pressure at C is

- (1) 3.284 atm (2) 1.642 atm
(3) 1.0821 atm (4) 1.821 atm

64. Work done in the process $C \rightarrow A$ is

- (1) 20.0 L-atm (2) 8.21 L-atm
(3) 26.2 L-atm (4) 25.0 L-atm

65. The process which occurs in going from, $B \rightarrow C$ is

- (1) Isothermal (2) Adiabatic
(3) Isobaric (4) Isochoric

66. The pressures at A and B in the atmosphere are, respectively,

- (1) 0.821 and 1.642 (2) 1.642 and 2
(3) 2 and 3 (4) 3 and 4

Paragraph 14

The thermodynamic property that measures the extent of molecular disorder is called entropy. Entropy change of phase transformation can be calculated using Trouton's formula ($\Delta S = \Delta H/T$). In the reversible adiabatic process, however, ΔS will be zero. The rise in temperature in isobaric and isochoric conditions is found to increase the randomness or entropy of the system.

$$\Delta S = 2.303C \log(T_1/T_2)$$

67. The entropy change in an adiabatic process is

- (1) Zero (2) Positive
(3) Negative (4) Remains same

68. If water in an insulated vessel at -10°C suddenly freezes, the entropy change of the system will be

- (1) $+20 \text{ J K}^{-1} \text{ mol}^{-1}$
(2) $-10 \text{ J K}^{-1} \text{ mol}^{-1}$
(3) Zero
(4) Same to that of surroundings

69. The melting point of a solid is 200 K and its latent heat of fusion is 400 cal mol^{-1} . The entropy change for the fusion of 1 mole of the solid (in cal K^{-1}) at the same temperature would be

- (1) 800 (2) 2 (3) 0.2 (4) 80

70. For which of the following cases, $\Delta S = \frac{\Delta H}{T}$?

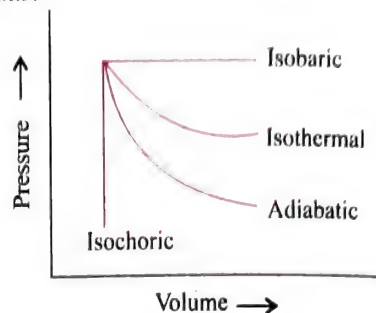
- (1) A process of which $\Delta C_p = 0$, but $\Delta C_v = 0$
(2) An isothermal process
(3) An isobaric process
(4) An isothermal reversible phase transition process

71. When 1 mol of an ideal gas is compressed to half of its volume, its temperature becomes double. Then the change in entropy (ΔS) would be

- (1) $C_p \ln 4$ (2) $C_p \ln 2$
(3) $C_p R \ln 4$ (4) $(C_p - R) \ln 4 \times C_p$

Paragraph 15

The pressure-volume of various thermodynamic processes is shown in graphs:



Work is the mode of transference of energy. It has been observed that reversible work done by the system is the maximum obtainable work.

$$w_{\text{rev}} > w_{\text{irr}}$$

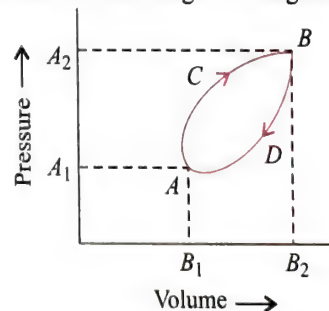
The works of isothermal and adiabatic processes are different from each other.

$$\begin{aligned} w_{\text{isothermal reversible}} &= 2.303nRT \log_{10} \left(\frac{V_2}{V_1} \right) \\ &= 2.303nRT \log_{10} \left(\frac{P_2}{P_1} \right) \end{aligned}$$

$$w_{\text{adiabatic reversible}} = C_p(T_1 - T_2)$$

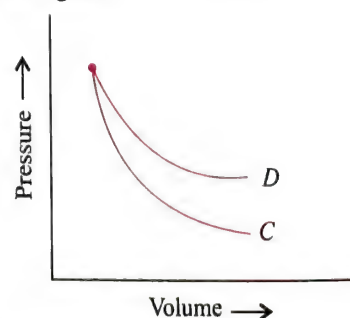
72. If w_1, w_2, w_3 , and w_4 are work done in isothermal, adiabatic, isobaric, and isochoric reversible processes, respectively then the correct sequence (for expansion) would be

- (1) $w_1 < w_2 < w_3 < w_4$ (2) $w_3 = w_2 = w_1 = w_4$
(3) $w_3 < w_2 < w_4 < w_1$ (4) $w_3 > w_1 > w_2 > w_4$

73. A thermodynamic system goes in a cyclic process as represented in the following P - V diagram:

The network done during the complete cycle is given by the area

- (1) Cycle ACBDA (2) AA_2B_2BDA
(3) AA_2B_2B (4) Area not bounded by curve

74. P - V plots for two gases during adiabatic processes are given in the given figure:

Plot D and Plot C should correspond to

- (1) He and O_2 (2) He and Ar
(3) O_2 and He (4) O_2 and N_2

7. The q value and work done in isothermal reversible expansion of one mole of an ideal gas from initial pressure of 1 bar to final pressure of 0.1 bar at constant temperature 273 K are:

- (1) 5.22 kJ, -5.22 kJ (2) +6.22 kJ, 6.22 kJ
(3) 5.22 J, 5.22 J (4) -6.22 J, -6.22 J

8. Calculate work done when 1 mole of an ideal gas is expanded reversibly from 30 L to 60 L at a constant temperature of 300 K

- (1) 8.78 kJ (2) -1.73 kJ
(3) 10.73 kJ (4) -9.78 kJ

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

Column I	Column II
a. For spontaneous reaction	p. $\Sigma(\text{BE})_R - \Sigma(\text{BE})_P$
b. For endothermic reaction	q. $\Delta H = \Delta U$
c. Bond dissociation energy	r. $\Delta G = -ve$
d. For solids and liquids in a thermochemical reaction	s. $\Sigma H_P > \Sigma H_R$

Column I	Column II
a. $\left(\frac{\partial U}{\partial V}\right)_T = 0$	p. Isothermal process
b. $W = -\Delta U$	q. $-nFE^\ominus$
c. $\Delta U = 0$	r. Adiabatic reaction
d. ΔG^\ominus	s. van der Waals gas
e. $\left(\frac{\partial T}{\partial P}\right)_H \neq 0$	t. Ideal gas

Column I	Column II
a. Joule-Thomson coefficient	p. $\left(\frac{\partial U}{\partial V}\right)_T = 0$
b. Kirchhoff's equation	q. $\left(\frac{2a}{RT} - b\right) = 0$
c. Ideal gas	r. $\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$
d. Inversion temperature	s. $\left(\frac{\partial T}{\partial P}\right)_H = \frac{-(\partial H / \partial P)_T}{C_P}$

Column I	Column II
a. $\Delta H = q_P$	p. $\Delta S^\ominus = 0$
b. Kirchhoff's equation	q. State function
c. $\text{H}^\oplus(\text{aq})$	r. Path function
d. Spontaneous process	s. $\Delta G > 0$
	t. $\Delta_{\text{total}} S^\ominus > 0$
	u. $\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1)$

Column I (Reaction)	Column II (Process)
a. $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$	p. Combustion
b. $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	q. Neutralisation
c. $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}$	r. Process of formation
d. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$	s. Used in fuel cell

Column I	Column II
a. $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$	p. Trouton equation
b. $\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V$	q. Effect of temperature on the heat of reaction
c. $\frac{\Delta_{\text{fusion}} H}{T_{\text{mp}}} = \Delta_{\text{fusion}} S$	r. Kirchhoff's equation
d. $\lim_{T \rightarrow 0\text{K}} S \rightarrow 0$	s. Third law of thermodynamics

Column I	Column II
a. $(\text{Heat of formation})_{\text{exp}} - (\text{Heat of formation})_{\text{calculated}}$	p. Heat of reaction
b. $\Sigma(\text{BE})_{\text{Reactants}} - \Sigma(\text{BE})_{\text{Products}}$	q. Resonance energy
c. $\Sigma(\text{Heat of combustion})_{\text{Reactants}} - \Sigma(\text{Heat of combustion})_{\text{Products}}$	r. ΔH
d. $C_P \Delta T$	s. Used in calorimetric method

Column I	Column II
a. Amount of heat required to raise the temperature of 1 mol substance by 1°C	p. Specific heat \times Molar mass
b. $\frac{\Delta H}{\Delta T}$ or $\frac{\Delta U}{\Delta T}$	q. Heat capacity = C , C_P , or C_V
c. Heat evolved in the combustion of 1 g of a substance	r. Electron gain enthalpy
d. Heat evolved when an extra electron is added to valence shell of an isolated gaseous atom	s. Calorific value

Column I	Column II
a. $\Delta_{\text{total}} S > 0$	p. w_{useful} done by system.
b. $\Delta_{\text{total}} S < 0$	q. Second law of thermodynamics
c. ΔH	r. Non-spontaneous
d. $-\Delta G$	s. $\Delta U > \Delta nRT$

10. Column I	Column II
a. Hess' law	p. $2.303 \log \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$
b. Combustion reaction	q. $\Delta_{\text{vap}} H = 88 \text{ J K}^{-1} \text{ mol}^{-1}$ × Boiling point in Kelvin
c. Trouton's law	r. Exothermic
d. Clausius–Clapeyron equation	s. ΔH remains the same irrespective steps

11. Column I	Column II
a. Enthalpy	p. Intrinsic property
b. Temperature	q. Path function
c. Free energy	r. Function of U, P, V
d. Work	s. State function

12. Column I	Column II
a. Temperature of a system always decreases	p. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
b. $\left(\frac{\partial U}{\partial V} \right)_T = 0$	q. Internal energy increases
c. Temperature of the system increases	r. Ideal gas
d. $\Delta H_{\text{hydrogenation (experimental)}} < \Delta H_{\text{hydrogenation (calculated)}}$	s. Adiabatic expansion

13. Column I	Column II
a. $\Delta U = 0, \Delta H = 0$	p. $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{CH}_3(\text{g})$
b. $\Delta H = -\text{ve}$	q. For reversible process
c. $\Delta_{\text{univ}} S = 0$	r. Non ideal solutions with negative
d. $\Delta G_{\text{mix}} = -\text{ve}$	s. For an ideal gas undergoing expansion isothermally

14. Column I	Column II
a. $\Delta_{\text{sys}} S > 0$ (Isolated system)	p. Spontaneous
b. $\Delta G < 0$	q. Non-spontaneous photochemical reaction
c. $\Delta_{\text{Total}} S = 0$	r. Equilibrium
d. $(\Delta G)_{TP} > 0$	s. Non-spontaneous

15. Column I	Column II
a. Isothermal process (reversible)	p. $w = 2.303nRT \log \left(\frac{P_1}{P_2} \right)$
b. Adiabatic process	q. $PV^\gamma = \text{constant}$

c. $w = \frac{nR}{\gamma - 1} (T_2 - T_1)$	r. $w = 2.303nRT \log \left(\frac{V_2}{V_1} \right)$
d. Irreversible isothermal process	s. $w = -P_{\text{ext}} (V_2 - V_1)$

16. Column I (Quantity)	Column II (Relation)
a. ΔG	p. $-nFE$ or $-nFE^\ominus$
b. ΔG^\ominus	q. $\Delta H - T \Delta S$
c. w or w_{max}	r. $-RT \log_e k$
d. ΔS^\ominus	s. $2.303nR \log_{10} \left(\frac{V_2}{V_1} \right)$

17. Column I (Gas)	Column II (Thermodynamic property)
a. O_2	p. $\gamma = 1.4$
b. N_2	q. $C_P = \frac{7}{2}R$
c. CO_2, CH_4	r. $\frac{23}{6}R$
d. 1 mol $\text{O}_2 + 2$ mol O_3	s. $\gamma = 1.33$

Here: C_P = Heat capacity at constant pressure
 $\gamma = C_P/C_V$

18. Column I (Reaction)	Column II (Relation)
a. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	p. $\Delta H = \Delta U + RT$
b. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$	q. $\Delta H = \Delta U$
c. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	r. $\Delta H = \Delta U - 2RT$
d. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	s. Forward shift by increasing pressure

19. Column I (Reaction)	Column II (Relation)
a. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$	p. $\Delta S = 0$
b. $2\text{KI}(\text{aq}) + \text{HgI}_2(\text{aq}) \rightarrow \text{K}_2[\text{HgI}_4](\text{aq})$	q. $\Delta S < 0$
c. $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g})$	r. $\Delta H > 0$
d. $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{g})$	s. $\Delta H < 0$

20. Column I	Column II
a. O_2	p. $\gamma = 1.4$
b. N_2	q. $C_P = \frac{7}{2}R$
c. CO_2	r. $C_V = \frac{17}{6}R$
d. 1 mol $\text{O}_2 + 2$ mol O_3	s. $\gamma = 1.33$

Column I	Column II
a. Isothermal process (reversible)	p. $w = 2.303nRT \log \left(\frac{P_1}{P_2} \right)$
b. Adiabatic process (reversible)	q. $w = 0$
c. Adiabatic free expansion	r. $w = 2.303nRT \log \left(\frac{V_2}{V_1} \right)$
d. Isothermal free expansion	s. $w = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$

Column I	Column II
a. The amount of energy which must be invested in reaction to get it started.	p. Chemical equilibrium
b. A state in which the rate of forward reaction is exactly equal to the rate of the reverse reaction.	q. Activation energy
c. A process or reaction which consumes heat.	r. Endothermic
d. A process or reaction that releases heat.	s. Exothermic
	t. Threshold Energy

Column I	Column II
a. Exothermic	p. $H_P - H_R$
b. Endothermic	q. ΔH is negative
c. Spontaneous	r. ΔH is positive
d. Heat of reaction	s. ΔG is negative

Column I	Column II
a. Gibbs-Helmholtz reaction	p. Degree of randomness
b. First law of thermodynamic	q. $\Delta H = \Delta U + P \Delta V$
c. Enthalpy at constant pressure	r. Law of conservation of energy
d. Entropy	s. $\Delta G = \Delta H - T \Delta S$

Column I	Column II
a. A process carried out infinitesimally slowly	p. Adiabatic
b. A process in which no heat enters or leaves the system	q. $\Delta G = 0$
c. A process carried out at constant temperature	r. Sublimation
d. A process in equilibrium	s. $\Delta U = 0, \Delta H = 0$
e. $A(s) \rightarrow A(g)$	t. Reversible
f. Cyclic process	u. Isothermal

Column I (Thermodynamic properties)	Column II (Relation)
a. ΔG	p. $-RT \log K$
b. ΔH°	q. $RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_P$
c. ΔS°	r. $-nFE$
d. ΔG°	s. $-\left(\frac{\partial \Delta G}{\partial T} \right)_P$

Column I	Column II
a. Spontaneous process	p. $\Delta H = -ve$
b. Heat flow from high temperature of system towards low temperature of surroundings	q. $\Delta G = +ve$
c. Exergonic process	r. $\Delta_{\text{total}} S = +ve$
d. Increase in the randomness of system by heating	s. $\Delta G = -ve$

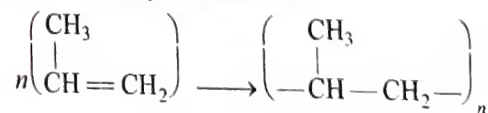
Numerical Value Type

1. $\Delta_f H^\circ$ of Cyclohexene (l) and benzene at 25°C is -156 and $+46 \text{ kJ mol}^{-1}$, respectively. $\Delta_{\text{hydrogenation}} H^\circ$ of cyclohexene (l) at 25°C is -119 kJ mol^{-1} .

Resonance energy of benzene is found to be $-38x \text{ kJ mol}^{-1}$. Find the value of x .

2. Bond dissociation energy of XY , X_2 , and Y_2 (all diatomic molecules) are in the ratio of $1:1:0.5$ and ΔH_f° of XY is -100 kJ mol^{-1} . The bond dissociation energy of X_2 is $100x$. Find the value of x .

3. The polymerisation of propene to linear polypropene is represented by the reaction



where n has large integral value, the average enthalpies of bond dissociation for $(\text{C}=\text{C})$ and $(\text{C}-\text{C})$ at 298K are $+590$ and $+331 \text{ kJ mol}^{-1}$, respectively. The enthalpy of polymerisation is -360 kJ mol^{-1} . Find the value of n .

4. $\Delta_f H^\circ$ of hypothetical MgCl is -125 kJ mol^{-1} and for MgCl_2 is -642 kJ mol^{-1} . The enthalpy of disproportionation of MgCl is $-49x$. Find the value of x .
5. The lattice energy of solid KCl is $181 \text{ kcal mol}^{-1}$ and the enthalpy of solution of KCl in H_2O is $1.0 \text{ kcal mol}^{-1}$. If the hydration enthalpies of K^+ and Cl^- ions are in the ratio of $2:1$ then the enthalpy of hydration of K^+ is $-20x \text{ K cal mol}^{-1}$. Find the value of x .
6. A heated iron block at 127°C loses 300 J of heat to the surroundings which are at a temperature of 27° . This process is $0.05x \text{ J K}^{-1}$. Find the value of x .

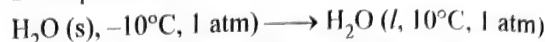
7. Amongst the following, the total number of reactions/processes in which the entropy increases are:

- $2\text{NaHCO}_3(\text{s}) \longrightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
 - A liquid crystallises into a solid.
 - Temperature of crystalline solid is raised from zero K to 100 K.
 - Hard boiling of an egg.
 - Devitrification of glass.
 - Stretching of a rubber band.
 - Desalination of water.
 - $\text{NH}_3(\text{g}, 10 \text{ atm}) \longrightarrow \text{NH}_3(\text{g}, 1 \text{ atm})$
8. Amongst the following, the total number of physical properties which are extensive are:

- Density
- Viscosity
- Surface tension
- Dipole moment
- Volume
- Refractive index
- ΔG
- ΔH
- ΔU
- ΔS

9. Amongst the following in Q. 8 above, mention the total number of intensive physical properties.

10. In the process:



C_p for ice = $9 \text{ cal deg}^{-1} \text{ mol}^{-1}$, C_p for H_2O = $18 \text{ cal deg}^{-1} \text{ mol}^{-1}$. Latent heat of fusion of ice = $1440 \text{ cal mol}^{-1}$ at 0°C . The entropy change for the above process is $6.258 \text{ cal. deg}^{-1} \text{ mol}^{-1}$.

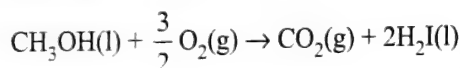
Give the total number of steps in which the third law of thermodynamics is used.

Archives

JEE MAIN

Single Correct Answer Type

1. In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

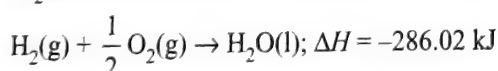


At 298 K standard Gibbs energies of formation for $\text{CH}_3\text{OH}(\text{l})$, $\text{H}_2\text{O}(\text{l})$, and $\text{CO}_2(\text{g})$ are -166.2 , -237.2 , and $-394.4 \text{ kJ mol}^{-1}$, respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be

- 80%
- 87%
- 90%
- 97%

(AIEEE 2009)

2. On the basis of the following thermochemical data [$\Delta_f G^\circ \text{H}^-(\text{aq}) = 0$]



The value of enthalpy of formation of OH^- ion at 25°C is

- -22.88 kJ
- -228.88 kJ
- -228.88 kJ
- -343.52 kJ

(AIEEE 2009)

3. The standard enthalpy of formation of NH_3 is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N-H bond in NH_3 is

- -964 kJ mol^{-1}
- $+352 \text{ kJ mol}^{-1}$
- $+1056 \text{ kJ mol}^{-1}$
- $-1102 \text{ kJ mol}^{-1}$

(AIEEE 2010)

4. For a particular reversible reaction, at temperature T , ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

- $T_e > T$
- $T > T_e$
- T_e is 5 times T
- $T = T_e$

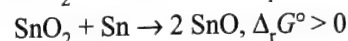
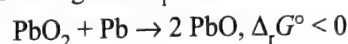
(AIEEE 2010)

5. The entropy change involved in the isothermal reversible expansion of 2 mole of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is

- $38.3 \text{ J mol}^{-1} \text{ K}^{-1}$
- $35.8 \text{ J mol}^{-1} \text{ K}^{-1}$
- $32.3 \text{ J mol}^{-1} \text{ K}^{-1}$
- $42.3 \text{ J mol}^{-1} \text{ K}^{-1}$

(AIEEE 2011)

6. In view of the signs of $\Delta_r G^\circ$ for the following reactions

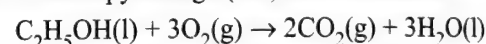


Which oxidation states are more characteristic for lead and tin?

- For lead + 4, for tin + 2
- For lead + 2, for tin + 2
- For lead + 4, for tin + 4
- For lead + 2, for tin + 4

(AIEEE 2011)

7. The value of enthalpy change (ΔH) for the reaction

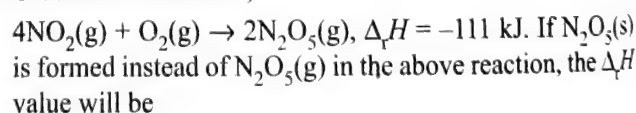


at 27°C is $-1366.5 \text{ kJ mol}^{-1}$. The value of internal energy change for the above reaction at this temperature will be

- -1371.5 kJ
- -1369.0 kJ
- -1364.0 kJ
- -1361.5 kJ

(AIEEE 2011)

8. Consider the reaction,



- -165 kJ
- $+54 \text{ kJ}$
- $+219 \text{ kJ}$
- -219 kJ

(AIEEE 2011)

9. The incorrect expression among the following is

$$(1) \frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$$

(2) in isothermal process,

$$W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$$

$$(3) \ln K = \frac{\Delta H - T\Delta S^\circ}{RT}$$

$$(4) K = e^{-\Delta G^\circ/RT}$$

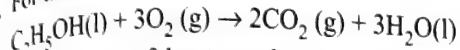
(AIEEE 2012)

10. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be ($R = 8.314 \text{ J/mol K}$, $\ln 7.5 = 2.01$)

- (1) $q = +208 \text{ J}$, $W = -208 \text{ J}$
 (2) $q = -208 \text{ J}$, $W = -208 \text{ J}$
 (3) $q = -208 \text{ J}$, $W = +208 \text{ J}$
 (4) $q = +208 \text{ J}$, $W = +208 \text{ J}$

(JEE Main 2013)

11. For the complete combustion of ethanol,

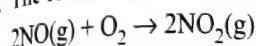


the amount of heat produced as measured in bomb calorimeter is $1364.47 \text{ kJ mol}^{-1}$ at 25°C. Assuming ideality, the enthalpy of combustion, $\Delta_c H$ for the reaction will be [$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$]

- (1) $-1366.95 \text{ kJ mol}^{-1}$ (2) $-1361.95 \text{ kJ mol}^{-1}$
 (3) $-1460.50 \text{ kJ mol}^{-1}$ (4) $-1350.50 \text{ kJ mol}^{-1}$

(JEE Main 2014)

12. The following reaction is performed at 298 K



The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $\text{NO}_2(\text{g})$ at 298 K? ($K_p = 1.6 \times 10^{12}$)

- (1) $R(298) \ln(1.6 \times 10^{12}) - 86600$
 (2) $86600 + R(298) \ln(1.6 \times 10^{12})$
 (3) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$

- (4) $0.5 [2 \times 86,600 - R(298) \ln(1.6 \times 10^{12})]$

(JEE Main 2015)

13. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is

- (1) 32 (2) 64
 (3) 128 (4) 488

(JEE Main 2015)

14. The heats of combustion of carbon and carbon monoxide are -393.5 and $-285.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is:

- (1) -110.5 (2) 110.5
 (3) 676.5 (4) -676.5

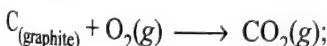
(JEE Main 2016)

15. ΔU is equal to:

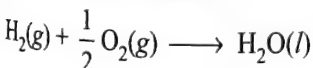
- (1) Isochoric work (2) Isobaric work
 (3) Adiabatic work (4) Isothermal work

(JEE Main 2017)

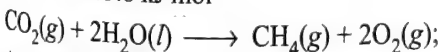
16. Given



$$\Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1}$$



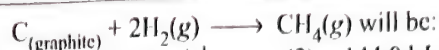
$$\Delta_f H^\circ = -285.8 \text{ kJ mol}^{-1}$$



$$\Delta_f H^\circ = +890.3 \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, the value of

$\Delta_R H^\circ$ at 298 K for the reaction



- (1) $+74.8 \text{ kJ mol}^{-1}$ (2) $+144.0 \text{ kJ mol}^{-1}$
 (3) $-74.8 \text{ kJ mol}^{-1}$ (4) $-144.0 \text{ kJ mol}^{-1}$

(JEE Main 2017)

17. The combustion of benzene (l) gives $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O(l)}$. Given that heat of combustion of benzene at constant volume is $-3263.9 \text{ kJ mol}^{-1}$ at 25°C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be - ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

- (1) -452.46 (2) 3260
 (3) -3267.6 (4) 4152.6

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. The bond energy (in kcal mol^{-1}) of a C—C single bond is approximately

- (1) 1 (2) 10 (3) 100 (4) 1000

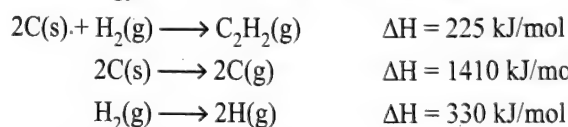
(IIT-JEE 2010)

2. The species which by definition has zero standard molar enthalpy of formation at 298 K is

- (1) $\text{Br}_2(\text{g})$ (2) $\text{Cl}_2(\text{g})$ (3) $\text{H}_2\text{O(g)}$ (4) $\text{CH}_4(\text{g})$

(IIT-JEE 2010)

3. Using the data provided, calculate the multiple bond energy (kJ/mol) of a $\text{C} \equiv \text{C}$ bond of C_2H_2 . That energy is (take the bond energy of a C—H bond as 350 kJ/mol)



- (1) 1165 (2) 837

- (3) 865 (4) 815 (IIT-JEE 2012)

4. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :

($R = 8.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$)

- (1) $q = -208 \text{ J}$, $w = -208 \text{ J}$ (2) $q = -208 \text{ J}$, $w = +208 \text{ J}$
 (3) $q = +208 \text{ J}$, $w = +208 \text{ J}$ (4) $q = +208 \text{ J}$, $w = -208 \text{ J}$

(JEE Advanced 2013)

5. The standard enthalpies of formation of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O(l)}$ and glucose (s) at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is

- (1) $+2900 \text{ kJ}$ (2) -2900 kJ
 (3) -16.11 kJ (4) $+16.11 \text{ kJ}$

(JEE Advanced 2013)

6. For complete combustion of ethanol,



the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C. Assuming ideality the enthalpy of combustion, $\Delta_c H$, for the reaction will be :

($R = 8.314 \text{ kJ mol}^{-1}$)

(1) $-1460.50 \text{ kJ mol}^{-1}$

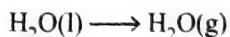
(2) $-1350.50 \text{ kJ mol}^{-1}$

(3) $-1366.95 \text{ kJ mol}^{-1}$

(4) $-1361.95 \text{ kJ mol}^{-1}$

(JEE Advanced 2014)

7. For the process

at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is

(1) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} > 0$

(2) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$

(3) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} > 0$

(4) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} < 0$

(JEE Advanced 2014)

8. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{sur}) in JK^{-1} is : (1 L atm = 101.3 J)

(1) 5.763

(2) 1.013

(3) -1.013

(4) -5.763

(JEE Advanced 2016)

9. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at $T = 298 \text{ K}$ are

$\Delta_f G^\circ [\text{C(graphite)}] = 0 \text{ kJ mol}^{-1}$

$\Delta_f G^\circ [\text{C(diamond)}] = 2.9 \text{ kJ mol}^{-1}$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. If C(graphite) is converted to C(diamond) isothermally at $T = 298 \text{ K}$, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information : $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$; $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$; $1 \text{ bar} = 10^5 \text{ Pa}$]

(1) 14501 bar

(2) 29001 bar

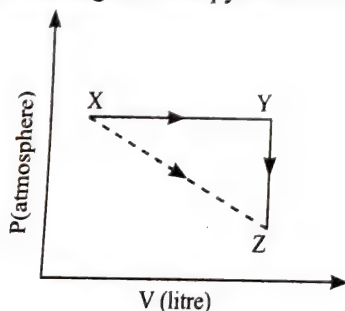
(3) 58001 bar

(4) 1405 bar

(JEE Advanced 2017)

Multiple Correct Answers Type

1. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choices is (are) correct?

[Take ΔS as change in entropy and w as work done].

(1) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$

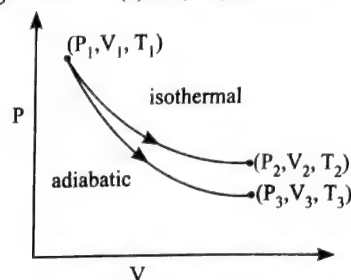
(2) $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$

(3) $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$

(4) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

(IIT-JEE 2012)

2. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct?



(1) $T_1 = T_2$

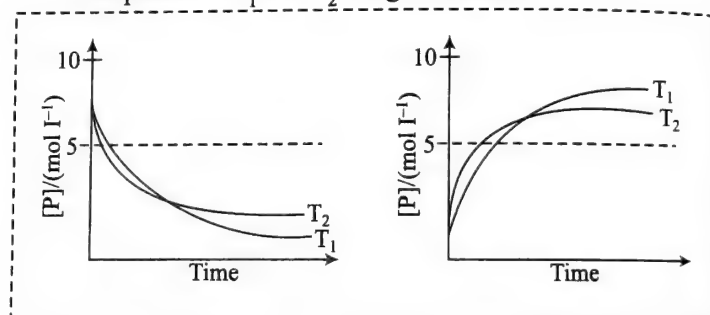
(2) $T_3 > T_1$

(3) $W_{\text{isothermal}} > W_{\text{adiabatic}}$

(4) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

(IIT-JEE 2012)

3. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ with time at temperatures T_1 and T_2 are given below.



If $T_2 > T_1$, the correct statement(s) is (are) (Assume ΔH° and ΔS° are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2/T_1 . Here H , S , G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively).

(1) $\Delta H^\circ < 0$, $\Delta S^\circ < 0$

(2) $\Delta G^\circ < 0$, $\Delta H^\circ > 0$

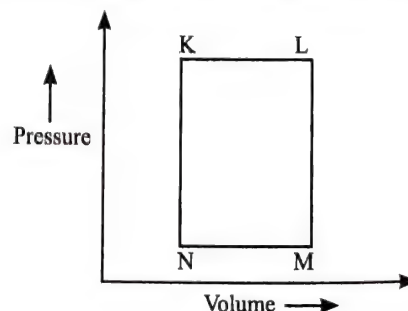
(3) $\Delta G^\circ < 0$, $\Delta S^\circ < 0$

(4) $\Delta G^\circ < 0$, $\Delta S^\circ > 0$

(JEE Advanced 2018)

Linked Comprehension Type**Paragraph 1**

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



1. The succeeding operation that enable this transformation of states are

- (1) Heating, cooling, heating, cooling
- (2) Cooling, heating, cooling, heating
- (3) Heating, cooling, cooling, heating
- (4) Cooling, heating, heating, cooling

2. The pair of isochoric processes among the transformation of states is

- (1) K to L and L to M
- (2) L to M and N to K
- (3) L to M and M to N
- (4) M to N and N to K

(JEE Advanced 2013)

Paragraph 2

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant ($-57.0 \text{ kJ mol}^{-1}$), this experiment could be used to measure the calorimeter constant.

In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

(Consider heat capacity of all solutions as $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ and density of all solutions as 1.0 g mL^{-1} .)

3. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is

- (1) 1.0
- (2) 10.0
- (3) 24.5
- (4) 51.4

4. The pH of the solution after Expt. 2 is

- (1) 2.8
- (2) 4.7
- (3) 5.0
- (4) 7.0

(JEE Advanced 2015)

Matrix Match Type

1. Match the transformation in column I with appropriate column II. (IIT-JEE 2011)

Column I	Column II
a. $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$	p. Phase transition
b. $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	q. Allotropic change
c. $2\text{H}^+ \rightarrow \text{H}_2(\text{g})$	r. ΔH is positive
d. $\text{P}_{(\text{white solid})} \rightarrow \text{P}_{(\text{red solid})}$	s. ΔS is positive
	t. ΔS is negative

2. Match the thermodynamic processes given under Column I with the expressions given under Column II.

Column I	Column II
a. Freezing of water at 273 K and 1 atm	(p) $q = 0$
b. Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(q) $w = 0$
c. Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(r) $\Delta S_{\text{sys}} < 0$
d. Reversible heating of $\text{H}_2(\text{g})$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(s) $\Delta U = 0$
	(t) $\Delta G = 0$

(JEE Advanced 2015)

Numerical Value Type

1. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , find the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} .

(IIT-JEE 2009)

2. The surface of copper gets tarnished by the formation of copper oxide, N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The vapour oxidises copper as per the reaction given below:
- $$2\text{Cu}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{Cu}_2(\text{s}) + \text{H}_2(\text{g})$$

$p\text{H}_2$ is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p\text{H}_2)$ is

(Given: total pressure = 1 bar, R (universal gas constant) = $8 \text{ JK}^{-1} \text{ mol}^{-1}$, $\ln(10) = 2.3$. Cu(s) and $\text{Cu}_2\text{O}(\text{s})$ are mutually immiscible.

At 1250 K: $2\text{Cu}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Cu}_2\text{O}(\text{g});$

$$\Delta G^0 = -78,000 \text{ J mol}^{-1}$$

$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta G^0 = -1,78,000 \text{ J mol}^{-1}; G$ is the Gibbs energy)

(JEE Advanced 2018)

Answers Key**EXERCISES****Single Correct Answer Type**

1. (2)
2. (2)
3. (1)
4. (3)
5. (4)
6. (3)
7. (1)
8. (2)
9. (4)
10. (3)
11. (4)
12. (1)
13. (3)
14. (2)
15. (3)
16. (2)
17. (3)
18. (3)
19. (3)
20. (2)

21. (2)
22. (2)
23. (2)
24. (4)
25. (3)
26. (3)
27. (2)
28. (4)
29. (3)
30. (2)
31. (2)
32. (3)
33. (3)
34. (2)
35. (3)
36. (2)
37. (2)
38. (4)
39. (1)
40. (4)
41. (1)
42. (4)
43. (4)
44. (3)
45. (3)
46. (2)
47. (3)
48. (1)
49. (2)
50. (2)

51. (1) 52. (1) 53. (2) 54. (3) 55. (1)
 56. (2) 57. (4) 58. (3) 59. (1) 60. (2, 4)
 61. (2) 62. (4)

Multiple Correct Answers Type

1. (2, 4) 2. (2, 3, 4) 3. (1, 3)
 4. (1, 2, 3) 5. (1, 2, 3) 6. (1, 3)
 7. (2, 3, 4) 8. (1, 2, 3, 4) 9. (1, 2, 3, 4)
 10. (2, 3, 4) 11. (2, 4) 12. (1, 3)
 13. (1, 2) 14. (4) 15. (1, 2, 3)
 16. (1, 2, 3) 17. (1, 2) 18. (1, 2, 3, 4)
 19. (1, 2, 3) 20. (1, 3) 21. (2, 3, 4)
 22. (1, 2) 23. (2, 3) 24. (2, 3, 4)
 25. (1, 2) 26. (1, 3) 27. (1, 2)
 28. (1, 2) 29. (1, 2) 30. (1, 2, 3)
 31. (2, 3, 4) 32. (1, 2, 3) 33. (1, 2, 4)
 34. (1, 3, 4) 35. (1, 2, 3, 4) 36. (1, 2)
 37. (1, 2, 3, 4) 38. (1, 2, 3, 4) 39. (1, 3)
 40. (1, 2, 3) 41. (2, 3, 5) 42. (2, 4)
 43. (3, 4) 44. (1, 3, 4) 45. (1, 2, 3)
 46. (2, 3) 47. (2, 4) 48. (1, 2, 4)
 49. (2, 3) 50. (1, 2, 3, 4) 51. (2, 3)
 52. (1, 2, 3)

Linked Comprehension Type

1. (2) 2. (1) 3. (3) 4. (4) 5. (1)
 6. (2) 7. (2) 8. (4) 9. (1) 10. (4)
 11. (2) 12. (2) 13. (4) 14. (2) 15. (1)
 16. (1) 17. (4) 18. (1) 19. (2) 20. (2)
 21. (4) 22. (2) 23. (2) 24. (1) 25. (2)
 26. (4) 27. (3) 28. (4) 29. (4) 30. (4)
 31. (2) 32. (3) 33. (2) 34. (3) 35. (3)
 36. (4) 37. (4) 38. (3) 39. (1) 40. (4)
 41. (3) 42. (1) 43. (4) 44. (2) 45. (3)
 46. (4) 47. (4) 48. (2) 49. (3) 50. (2)
 51. (1) 52. (2) 53. (2) 54. (2) 55. (1)
 56. (1) 57. (1) 58. (1) 59. (1) 60. (3)
 61. (4) 62. (2) 63. (2) 64. (2) 65. (3)
 66. (1) 67. (1) 68. (3) 69. (2) 70. (4)
 71. (2) 72. (4) 73. (1) 74. (3) 75. (1)
 76. (2)

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	r	s	p	q	—	—
2.	t	r	p	q	s	—
3.	s	r	p	q	—	—
4.	p	u	s	t	—	—
5.	p	p	q	p, r, s	—	—

6.	p, r	q, r	p	s	—	—
7.	q	p, r	p, r	p, r, s	—	—
8.	p, q	q, p	s	r	—	—
9.	q	r	s	p	—	—
10.	s	r	q	p	—	—
11.	r	p	r	q	—	—
12.	s	r	q	p	—	—
13.	s	p	q	r	—	—
14.	p	p, q	r	s	—	—
15.	p, r	q	q	s	—	—
16.	p, q	p, r	p	s	—	—
17.	p, q	p, q	s	s	—	—
18.	q	q	p	r, s	—	—
19.	p, q	q	q, r	q, s	—	—
20.	p, q	p, q	r	r	—	—
21.	p, r	s	q	q	—	—
22.	q	p	r	s	—	—
23.	q	r	s	p	—	—
24.	s	r	q	p	—	—
25.	t	p	u	q	r	s
26.	p, r	q	s	p, r	—	—
27.	r, s	p, r, s	q	q, r	—	—

Numerical Value Type

1. (4) 2. (4) 3. (5) 4. (8) 5. (6)
 6. (5) 7. (4) 8. (5) 9. (5) 10. (2)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (4) 2. (2) 3. (2) 4. (2) 5. (1)
 6. (4) 7. (3) 8. (1) 9. (3) 10. (1)
 11. (1) 12. (4) 13. (2) 14. (1) 15. (3)
 16. (3) 17. (3)

JEE Advanced**Single Correct Answer Type**

1. (3) 2. (2) 3. (4) 4. (4) 5. (3)
 6. (2) 7. (2) 8. (3) 9. (1)

Multiple Correct Answers Type

1. (1, 3) 2. (1, 4) 3. (1, 3)

Linked Comprehension Type

1. (3) 2. (2) 3. (1) 4. (2)

Matrix Match Type

1. (a \rightarrow p, r, s; b \rightarrow r, s; c \rightarrow t; d \rightarrow p, q, t)
 2. (a \rightarrow r, t; b \rightarrow p, q, s; c \rightarrow p, q, s; d \rightarrow s, t)

Numerical Value Type

1. (9) 2. (-14.6)

7

Chemical Equilibrium

OVERVIEW

1. **Law of mass action:** It was given by Guldberg and Waage. It is a theoretical concept which states that the rate of reaction is directly proportional to the product of molar concentration of reactants with each concentration term raised to the power equal to the stoichiometric coefficient of the species in the balanced equation.

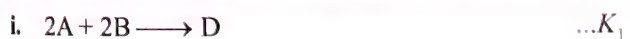
2. **Equilibrium constant (K):** It is the ratio of the velocity constants of forward reaction to that of backward reaction.

For an equilibrium: $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

3. **Stoichiometric representation of equilibrium constant**

	Chemical reaction	Equilibrium constant
a.	$A + B \rightleftharpoons C + D$	K_c
b.	$C + D \rightleftharpoons A + B$	$K_c = 1/K_c$
c.	$nA + nB \rightleftharpoons nC + nD$	$K_c = (K_c)^n$



Equation (iii) is obtained by subtracting equation (ii) from equation (i)

$$\therefore K = \frac{K_1}{K_2}$$



Equation (iii) is obtained by addition of equations (i) and (ii).

$$\therefore K = K_1 \times K_2$$

a. In equilibrium constant, if activities are used in place of molar concentrations, K becomes dimensionless (i.e., it has no units).

4. **Relationship between K_p , K_c , and K_x**

K_p (equilibrium constant in term of pressure)

$$\therefore K_p = K_c (RT)^{\Delta n}$$

$$\text{and } K_p = K_x (p)^{\Delta n}$$

$$\text{If } \Delta n = 0, \text{ then } K_p = K_c = K_x$$

$$\Delta n = +ve; \quad K_p > K_c; \quad K_p > K_x$$

$$\Delta n = -ve; \quad K_p < K_c; \quad K_p < K_x$$

5. **Degree of dissociation (α):** It is defined as the fraction of the total number of molecules dissociated into simpler molecules at particular temperature.

$$\text{or } \alpha = \frac{\text{Number moles dissociated}}{\text{Total number of moles taken}}$$

a. **Calculation of degree of dissociation from density measurements:**

$$\alpha = \frac{D - d}{(n - 1)d}$$

where d = observed vapour density at a particular temperature

D = Vapour density when there is no dissociation.

n = Number of molecules of products

$$\text{or } \alpha = \frac{M - m}{(n - 1)m}$$

Where, M = initial molecular mass

m = molecular mass at equilibrium

n = number of molecules of products

b. **Calculation of degree of dissociation using pressure-temperature relation:**

$$\alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

6. **Reaction quotient (Q):** The ratio of the product of molar concentration of the products to the product of molar concentrations of reactants with each concentration term raised to the power equal to the stoichiometric coefficient of that species is called reaction quotient.

At equilibrium, $Q = K$

At concentrations other than equilibrium, $Q \neq K$.

- If $Q > K_c$, the reaction will proceed in the direction reactants.
- If $Q < K$, the reaction will proceed in the product direction.
- If $Q = K_c$, the reaction is at equilibrium.

$$7. \log K_2 - \log K_1 = \frac{-\Delta H}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]. \text{ Here } T_2 > T_1$$

When $\Delta H = 0$, i.e., heat of reaction at constant volume is zero.

$$\Rightarrow K_2 = K_1$$

When $\Delta H = +ve$, i.e., endothermic reaction

$$\Rightarrow K_2 > K_1$$

When $\Delta H = -ve$, i.e., exothermic reaction

$$\Rightarrow K_2 < K_1$$

8. Equilibrium constant and standard free energy change:

$\Delta G = \Delta G^\ominus + 2.303 RT \log Q$, where Q = reaction quotient

At equilibrium $\Delta G = 0$ and $Q = K_p$ or K_c as the standard state is referred in terms of partial pressure or concentration.

Thus, at equilibrium,

$$\Delta G^\ominus = -2.303 RT \log K_c$$

$$\Delta G^\ominus = -2.303 RT \log K_p$$

Relation between ΔG^\ominus , K , and spontaneity

ΔG^\ominus	$\log K$	K	Reaction
Negative	Positive	> 1	Spontaneous
Positive	Negative	< 1	Non-spontaneous
0	0	$= 1$	Equilibrium

$$9. \Delta G^\ominus = -nFE^\ominus, \text{ where } E^\ominus \text{ standard emf of cell.}$$

10. **Le Chatelier's principle:** When an equilibrium is subjected to any change in concentration, temperature, or pressure, it shifts in a direction so as to undo the effect of change.

Factors influencing equilibrium concentrations:

a. Temperature:

- An increase in temperature for exothermic reactions decreases the concentration of products at equilibrium and vice-versa.
- An increase in temperature for endothermic reactions increases the concentration of products at equilibrium and vice-versa.

b. **Pressure:** An increase in pressure to an equilibrium favours the reaction where number of moles show a decrease and vice-versa.

Effect of pressure (or volume)

Type of reaction	Effect of pressure (or volume)
Type I: $\Delta n = 0$	Equilibrium is not affected
Type II: $\Delta n = +ve$	Increase in P (or decrease in V) shifts the equilibrium to left
$\Delta n = -ve$	Increase in P (or decrease in V) shifts the equilibrium to right

c. Addition of inert gas:

- Addition of inert gas to an equilibrium (if $\Delta n = 0$) has no effect.
- Addition of inert gas to an equilibrium (if $\Delta n \neq 0$) has no effect, if addition is made at constant

volume. But addition at constant pressure will favour the direction of reaction where total number of moles at equilibrium show an increase.

Effect of inert gas

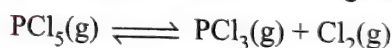
Condition		Effect
$\Delta V = 0$	$\Delta n = 0, +ve \text{ or } -ve$	No effect
$\Delta V \neq 0$	$\Delta n = 0$	No effect
$\Delta V \neq 0$	$\Delta n > 0$	Forward shift
$\Delta V \neq 0$	$\Delta n < 0$	Backward shift

11.

S. No.	Irreversible Reactions	Reversible Reactions
(i)	These take place in one direction only	These take place in both the directions.
(ii)	They almost go to completion.	They never go to completion.
(iii)	They do not attain equilibrium.	They attain equilibrium.
(iv)	The arrow between reactants and products indicates the direction of the reaction.	The sign \rightleftharpoons represents the reversible reaction.

12. Calculation of Degree of Dissociation Using Pressure-Temperature Determination:

Let us consider the following reaction:



Initial pressure and temperature are P_1 and T_1 . At equilibrium, pressure and temperature are P_2 and T_2 , respectively. The volume of vessel is constant, equal to ' V '.

	$\text{PCl}_5(\text{g})$	$\text{PCl}_3(\text{g})$	$\text{Cl}_2(\text{g})$	n	V	T	P
$t = 0$	a	0	0	a	V	T_1	P_1
t_{eq}	$a - \alpha\alpha$	$\alpha\alpha$	$\alpha\alpha$	$a + \alpha\alpha$	V	T_2	P_2

$$\text{Initial state } P_1 V = aRT_1 \quad \dots(i)$$

$$\text{Equilibrium state } P_2 V = (a + \alpha\alpha)RT_2 \quad \dots(ii)$$

Dividing equations (i) and (ii), we get

$$\frac{P_1}{P_2} = \frac{T_1}{(1 + \alpha)T_2}$$

$$(1 + \alpha) = \frac{T_1 P_2}{T_2 P_1}$$

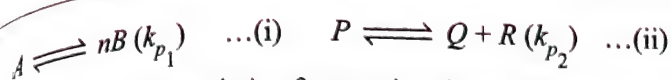
$$\therefore \alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

Alternatively:

$$\frac{\text{Initial moles}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure after change of temperature}}{\text{Equilibrium pressure}}$$

13. Direct relation between equilibrium constants (K_{p_1} and K_{p_2}) of two reactions and total pressures of two reaction (P_1 and P_2) when degree of dissociation (α) is same for both the reactions:

Let k_{p_1} and k_{p_2} are in the ratio of x and y for the two reactions.



The degree of dissociation for reaction (i) and (ii) are same, then the ratio of the total pressures (P_1 & P_2) for two reaction are,

$$\frac{K_{p_1}}{K_{p_2}} = \frac{x}{y} = \frac{(n)^n P_1}{P_2}$$

a. For example, for reactions, (iii) & (iv), $\frac{K_{p_1}}{K_{p_2}} = \frac{x}{y}$.

Considering degree of dissociation is same for both the reaction.



Then,

$$\frac{K_{p_1}}{K_{p_2}} = \frac{x}{y} = \frac{(2)^2 P_1}{P_2}$$

If K_{p_1}/K_{p_2} for reactions (iii) and (iv) are in the ratio of 1 : 3, then P_1/P_2 is,

$$\frac{K_{p_1}}{K_{p_2}} = \frac{1}{3} = \frac{(2)^2 P_1}{P_2}$$

$$\therefore \frac{P_1}{P_2} = \frac{1}{3 \times 4} = 1:12$$

b. If P_1/P_2 for reaction (iii) and (iv) are in the ratio of 2 : 3, then K_{p_1}/K_{p_2} (considering α is same for both the reaction), is,

$$\frac{K_{p_1}}{K_{p_2}} = \frac{x}{y} = \frac{(2)^2 P_1}{P_2} = \frac{4 \times 2}{3} = 8:3$$

$$\therefore \frac{x}{y} = \frac{K_{p_1}}{K_{p_2}} = 8:3$$

14. Some important points:

- Pure ice can be made to melt at a temperature slightly below 0°C by increasing the pressure. As the water so obtained on melting is below 0°C , it refreezes when pressure is reduced. It is called *regelation of ice*.
- Liquid water cannot exist beyond 647.15 K and 218 atmospheric pressure. These temperature and pressure are called *critical temperature* and *critical pressure* respectively. Beyond critical pressure and critical temperature only solid ice and water vapours can exist.
- In almost all cases melting point/freezing point is influenced by external pressure. Exception being only those solids and liquids which have same densities at their respective melting points.
- Increase in external pressure always increases the boiling point and vice-versa.

7.1 INTRODUCTION

It is observed that many of the chemical reactions do not proceed to completion. They proceed to some extent which implies that the reactants are not completely converted into the products.

When the reactants in a closed vessel at a particular temperature react to give products, the concentration of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations either the reactants or products. This stage of the system is called the *state of equilibrium*. At equilibrium state, the rates of forward reaction and backward reaction become equal.

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving O_2 molecules and the protein hemoglobin play a crucial role in the transport and delivery of O_2 from our lungs to muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO.

Equilibrium can be attained for both physical processes and chemical reactions. The equilibrium established in physical processes such as dissolution of salt, evaporation of water, etc., is called physical equilibrium, whereas the equilibrium established in chemical processes such as decomposition of ammonium chloride or reaction between hydrogen and iodine is called chemical equilibrium.

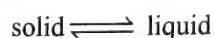
Based on the extent to which the reactions proceed to reach the state of *chemical equilibrium*, these may be classified in three groups.

- The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.
- The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.
- The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of a reaction in equilibrium varies with the experimental conditions such as the concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favourable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit.

7.2 EQUILIBRIUM IN PHYSICAL PROCESSES

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most common examples are phase transformation processes, e.g.,



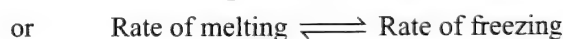
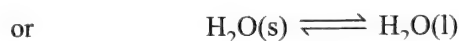
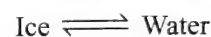
7.2.1 SOLID-LIQUID EQUILIBRIUM

When a pure solid substance is heated under atmospheric pressure, it gradually starts converting into the liquid at a certain temperature. At this particular temperature, the solid and liquid phases of the substance coexist with each other.

Thus, for any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases can coexist is called normal melting point or the normal freezing point of the substance.

At melting point, the substance in solid phase is in equilibrium with the liquid phase of the substance. However, if the mixture of solid and liquid at equilibrium is further heated, the solid is gradually converted to liquid while the temperature remains constant. If a solid-liquid system at melting point is taken in a perfectly insulated flask then this constitutes a system in which solid is in dynamic equilibrium with liquid.

For example, ice and water kept in a perfectly insulated thermos flask at 0°C and the atmospheric pressure are in equilibrium state. It is observed that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noted at the boundary between the ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change in the mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal. This represents a dynamic equilibrium between ice and water, i.e.,



From the above equilibrium, we can infer the following

- Both the opposing processes occur simultaneously
- Both the processes occur at the same rate so that the amount of ice and water remains constant.

7.2.2 LIQUID-VAPOUR EQUILIBRIUM

This equilibrium can be better understood if we consider the example of evaporation of water in a closed vessel.

Let us consider a transparent box carrying a U-tube with mercury (manometer). The box is evacuated with the help of vacuum pump connected to it and it is dried with drying agent such as anhydrous calcium chloride (or phosphorous pentoxide). After drying the box a watch glass containing water is placed inside the box. It is observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also, the volume of water in the watch glass decreases (Fig. 7.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to the addition of water

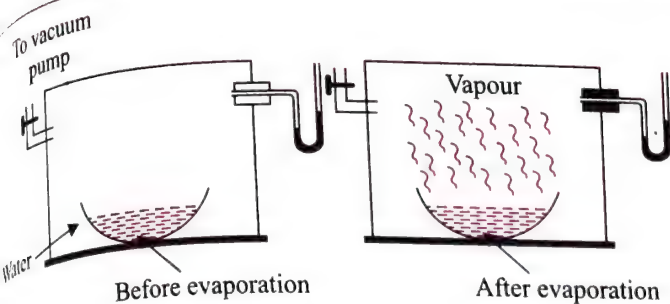
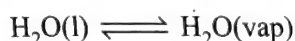


Fig. 7.1 Measuring equilibrium vapour pressure of water at a constant temperature

molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally, it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained, i.e.,

Rate of evaporation = Rate of condensation



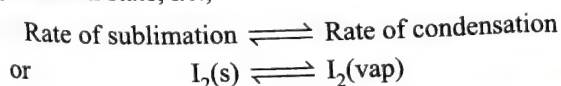
At equilibrium, the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature.

The vapour pressure of a liquid also depends on the nature of the liquid. A liquid having weaker intermolecular forces has higher vapour pressure. For example, acetone has higher vapour pressure than water. A liquid having greater vapour pressure is more volatile and has a lower boiling point. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence, the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

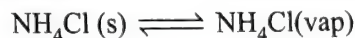
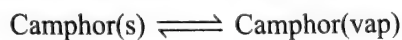
Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called the normal boiling point of the liquid. The boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases.

7.2.3 SOLID-VAPOUR EQUILIBRIUM

This equilibrium can be understood by considering the systems where solids sublime to vapour phase. For example, if we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After sometime, the intensity of colour becomes constant and at this stage the rate of sublimation of solid becomes equal to the rate of condensation of vapour into solid. This stage is referred to the equilibrium state, i.e.,



Other examples showing this kind of equilibrium are,



7.2.4 EQUILIBRIUM INVOLVING DISSOLUTION OF SOLID OR GASES IN LIQUIDS

Solids in liquids

We can dissolve only a limited amount of solid solute in a given amount of solvent. For example, if we dissolve sugar into water, initially the sugar crystal will dissolve into water but after some time no more sugar can be dissolved into water at room temperature.

A solution in which no more solute can be dissolved is called a saturated solution. The concentration of the solute in a saturated solution depends upon the temperature.

In a saturated solution, a dynamic equilibrium exists between the solute molecules in the solid state and in the solution, i.e.,

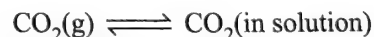


and the rate of dissolution of sugar is equal to the rate of crystallisation of sugar.

The dynamic nature of equilibrium can be confirmed with the help of radioactive sugar. If we add some radioactive sugar into saturated solution of non-radioactive sugar then after some time radioactivity is observed both in the solution and in the sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

7.2.5 GASES IN LIQUIDS

The best example of this type of equilibrium is that of a soda water. When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. At a given pressure, there is an equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid. This may be expressed as:



The amount of the gas dissolved is governed by Henry's law.

This law states that:

The mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

$$m \propto P$$

$$m = kP$$

where k is the proportional constant and depends upon the temperature. Thus, on increasing the temperature, the amount of dissolved gas decreases.

The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened,

some of the dissolved carbon dioxide gas escape to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere.

The result discussed above about the physical equilibria can be generalised as:

- solid \rightleftharpoons liquid equilibrium can coexist only at one temperature (melting point) at 1 atm (1.013) bar pressure. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.
- In liquid \rightleftharpoons vapour equilibrium, the pressure of the vapours above the liquid (i.e., the vapour pressure) is constant at constant temperature.
- In solid \rightleftharpoons solution equilibrium, the solubility of the solid in the solution is constant at constant temperature.
- In gas \rightleftharpoons solution equilibrium, the concentration of a gas in the liquid is proportional to the pressure (concentration) of the gas over the liquid.

These observations are summarised in Table 7.1.

Table 7.1 Some features of physical equilibria

Process	Conclusion
Liquid \rightleftharpoons Vapour $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$	$P_{\text{H}_2\text{O}}$ constant at given temperature
Solid \rightleftharpoons Liquid $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)}$	Melting point is fixed at constant pressure
Solute(s) \rightleftharpoons Solute(sol) Sugar(s) \rightleftharpoons Sugar(sol)	Concentration of solute in solution is constant at a given temperature
Gas(g) \rightleftharpoons Gas(aq) $\text{CO}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(aq)}$	$[\text{gas(aq)}]/[\text{gas(g)}]$ is constant at a given temperature $[\text{CO}_2\text{(aq)}]/[\text{CO}_2\text{(g)}]$ is constant at a given temperature

7.2.6 GENERAL CHARACTERISTICS OF EQUILIBRIA INVOLVING PHYSICAL PROCESSES

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

- Equilibrium is possible only in a closed system at a given temperature.
- Equilibrium is dynamic in nature, i.e., these are two opposing processes taking place at the same rate.
- At equilibrium, all the measurable properties of the system remain constant. For example, in case of evaporation of water, the vapour pressure of liquid becomes constant at equilibrium.
- When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameter at a given temperature. For example, for the dissolution of CO_2 in water, at equilibrium



$\frac{[\text{CO}_2\text{(aq)}]}{[\text{CO}_2\text{(g)}]}$ is constant at a given temperature.

This constant is called the equilibrium constant.

- The magnitude of the equilibrium constant represents the extent to which the process proceeds before equilibrium is attained. For example, greater the value of $\frac{[\text{CO}_2\text{(aq)}]}{[\text{CO}_2\text{(g)}]}$ (equilibrium constant), greater is the extent to which CO_2 dissolves in water.

7.3 EQUILIBRIUM IN CHEMICAL PROCESSES

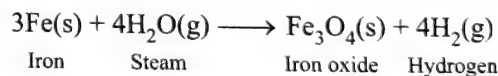
In the various processes described earlier involving physical changes, the two opposing processes take place, the rates of which becomes equal when equilibrium is attained.

Analogous to the physical systems, chemical reactions also attain a state of equilibrium. When opposing processes take place in a chemical reaction, the reaction is said to be a reversible reaction. In other words, a reaction that takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction. It is represented by putting a double arrow (\rightleftharpoons) between the reactants and the products, one arrow pointing towards the products and the other pointing towards the reactants. For example, a reversible reaction between *A* and *B* to form *C* and *D* will be represented as

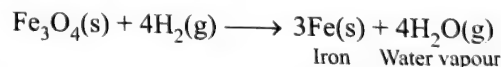


The concept of reversibility in a chemical reaction may be explained with the help of the following example:

If pieces of iron are placed in an open glass tube heated from below and steam is passed from the other end, the following reaction takes place:



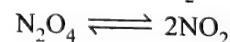
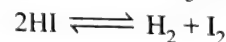
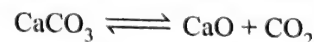
Again if in place of iron, iron oxide (Fe_3O_4) is placed in the tube, heated from below and hydrogen is passed over it, the following reaction takes place:

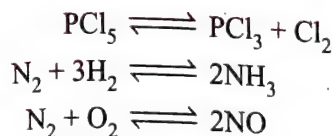


Since in the above case, the tube was open, hydrogen in the first case and water vapour in the second case escape out. However, if the tube is closed, both the reactions take place simultaneously and hence reaction becomes reversible. It may be represented as



Some more examples of reversible reactions are given below





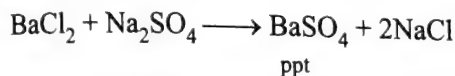
7.3.1 IRREVERSIBLE REACTIONS

The chemical reaction in which the products do not react under any condition to give back reactants, i.e., the reaction moves only in one direction or only in forward direction is called irreversible reactions.

Irreversible reactions are represented by putting a single arrow between the reactants and products, pointing from reactants towards products, i.e.



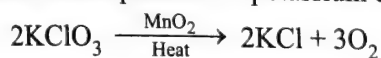
For example, when solutions containing equimolar concentrations of barium chloride and sodium sulphate are mixed, reaction occurs and practically whole of barium is precipitated as barium sulphate.



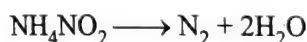
The reaction between BaSO_4 and NaCl , i.e., backward reaction, is not possible under the experimental conditions.

Some more examples of irreversible reactions are given below.

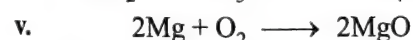
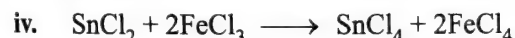
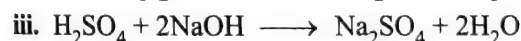
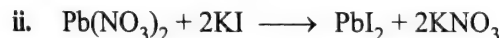
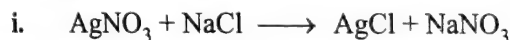
a. i. Thermal decomposition of potassium chlorate,



ii. Decomposition of ammonium nitrite:



b. Precipitation reactions,



7.3.2 CONCEPT OF CHEMICAL EQUILIBRIUM

Let us consider a general case of a reversible reaction



With passes of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 7.2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction.

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.

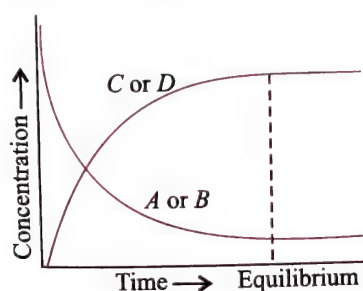


Fig. 7.2 Attainment of chemical equilibrium

Similarly, the reaction can reach the state of equilibrium even if we start with only C and D , that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The variation of the reaction rates with time and ultimately the attainment of chemical equilibrium may be represented diagrammatically as shown in Fig. 7.3.

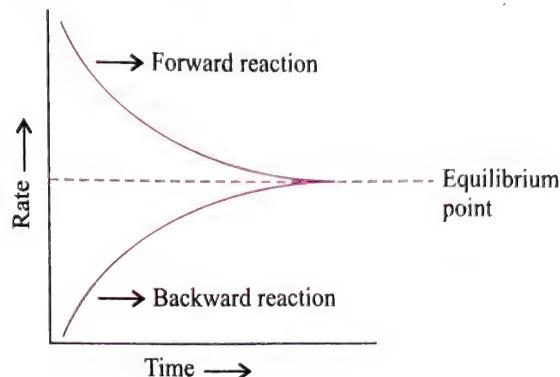
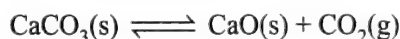


Fig. 7.3 Variation in reaction rates for the forward and backward reaction with time

The following examples illustrate the state of equilibrium in some reversible processes.

a. Decomposition of calcium carbonate

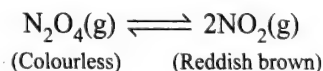
Calcium carbonate when heated to 1073 K in a closed evacuated vessel starts decomposing to yield calcium oxide and carbon dioxide gas as shown below



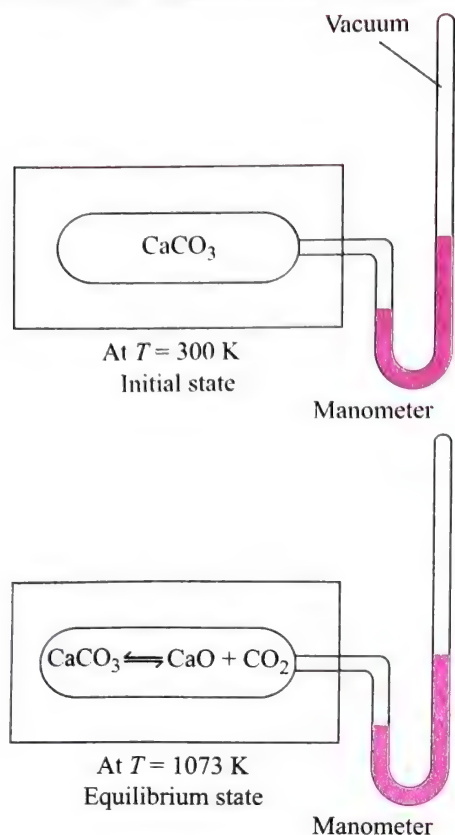
Carbon dioxide builds up pressure within the vessel which can be measured on a manometer, as shown in Fig. 7.4. The pressure goes on increasing as the reaction proceeds and finally becomes constant and remains so as long as the temperature remains constant. It appears that the reaction has stopped although CaCO_3 is still present. This indicates that the system has attained the equilibrium state.

b. Decomposition of N_2O_4 in a closed vessel

The decomposition of N_2O_4 in a closed vessel is a reversible reaction as represented below.

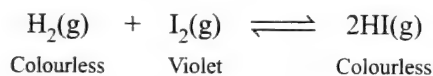


N_2O_4 is almost stable at 0°C and is almost colourless. Thus, if N_2O_4 is taken in a glass bulb which is then sealed and placed in ice, it is almost colourless. Now if the sealed glass bulb is shifted into a vessel containing water at 25°C , the bulb starts acquiring brown colour which first deepens and then becomes constant. This indicates a state of equilibrium in which the concentrations of N_2O_4 and NO_2 have become constant. That both are present in the reaction mixture can be tested by increasing the temperature of the bulb further when brown colour deepens (indicating more dissociation of N_2O_4) and by cooling the bulb down from 25°C when the brown colour fades (indicating combination of NO_2 molecules to form N_2O_4).

Fig. 7.4 Equilibrium in the decomposition of CaCO_3

c. Reaction between hydrogen and iodine

When hydrogen and iodine is heated in a closed vessel at 717 K, they react to form hydrogen iodide, reaction can be represented as



The colour of the reaction mixture is deep violet in the initial state due to the presence of iodine. As the reaction progresses, the intensity of colour decreases due to the formation of hydrogen iodide which is colourless.

After sometime, the intensity of colour becomes constant. This indicates that the reaction has attained a state of equilibrium.

7.3.3 DYNAMIC NATURE OF CHEMICAL EQUILIBRIUM

When the equilibrium is attained in a chemical reaction all the observable properties of the system become constant, for example, concentration of various species of reaction mixture.

For example, in the reaction between H_2 and I_2 to form HI , the intensity colour becomes constant because the concentrations of H_2 and I_2 and HI become constant. It may lead us to think that the reaction stops altogether at equilibrium. But this is not true. At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction so that there is no net change in the concentration of various species. In other words, the equilibrium state is a dynamic balance between the forward and the backward reaction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature

and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 7.5 shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using D_2 (deuterium) in place of H_2 . The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3 . After the equilibrium is attained, these two mixtures

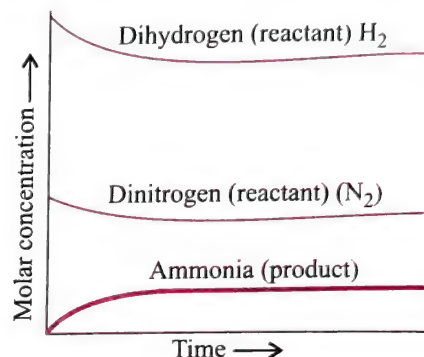
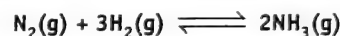


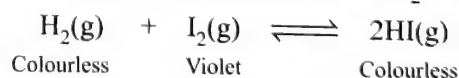
Fig 7.5 Depiction of equilibrium for the reaction



(H_2 , N_2 , NH_3) and (D_2 , N_2 , ND_3) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3 , NH_2D , NHD_2 , and ND_3) and dihydrogen and its deuterated forms (H_2 , HD , and D_2) are present. Thus, one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.

Similarly, in the reaction between H_2 and I_2 to form HI



If we start with initial concentration of H_2 and I_2 , the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases, while that of HI increases, until all of these become constant at equilibrium (Fig. 7.6). Accordingly to the concentration, the intensity of colour decreases initially and at equilibrium the colour intensity becomes constant. We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached (Fig. 7.6). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

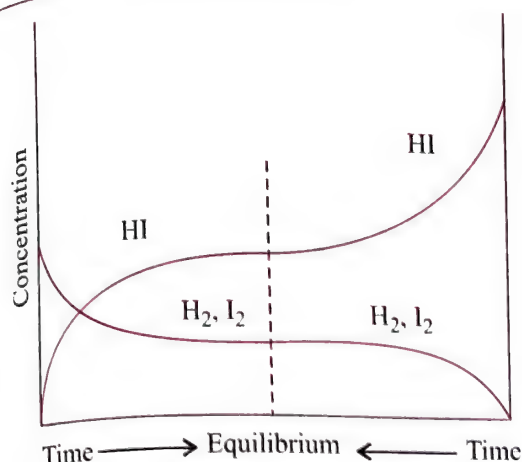


Fig. 7.6 Chemical equilibrium in the reaction

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ can be attained from either direction

3.4 CHARACTERISTIC OF CHEMICAL EQUILIBRIUM

The important characteristic of chemical equilibrium are as follows:

- The observable properties of the system such as concentration colour, pressure, etc., becomes constant at equilibrium.
- The equilibrium can be attained only if the system is closed.
- At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and therefore the equilibrium is dynamic in nature.
- Chemical reaction can be established from either direction, i.e., from the reactant direction as well as from the products direction.
- A catalyst does not alter the state of equilibrium.

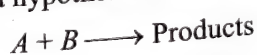
In reversible reaction, catalyst increases the rate of forward reaction as well as rate backward reaction to the same extent. Hence, the equilibrium is not altered. The only effect adding the catalyst is that the equilibrium is attained earlier.

7.4 LAW OF MASS ACTION AND EQUILIBRIUM CONSTANT

In 1864, two Norwegian chemists Cato Gulberg and Peter Waage put forward a law concerning a qualitative relationship between rates of reaction and the concentration of the reacting species. This law is known as *law of mass action*. This law states that at constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of reacting species with each concentration term raised to the power of stoichiometric coefficient of that species in the chemical equation.

Mathematical expression:

Let us consider a hypothetical reaction



According to the law of mass action,

$$\text{Rate of reaction } (r) \propto [A][B]$$

$$\text{or } r = k[A][B]$$

where $[A]$ and $[B]$ are the molar concentrations of the reactants A and B , respectively. k is the constant of proportionality called rate constant.

For any general reaction,



$$\text{The rate of reaction} \propto [A]^a[B]^b[C]^c[D]^d \dots$$

$$\text{or rate} = k[A]^a[B]^b[C]^c[D]^d \dots$$

7.4.1 APPLICATION OF THE LAW OF MASS ACTION TO CHEMICAL EQUILIBRIUM

The law of chemical equilibrium is a result obtained by applying the law of mass action to a reversible reaction in equilibrium.

Let consider a general reversible reaction



At equilibrium, according to the law of mass action

$$\text{Rate of forward reaction} \propto [A][B] = K_f[A][B]$$

where K_f is the proportionality constant called the *rate constant for the forward reaction*. $[A]$ and $[B]$ are molar concentrations of reactants A and B , respectively.

$$\text{Similarly, the rate of backward reaction} \propto [C][D] = K_b[C][D]$$

where K_b is the *rate constant for the backward reaction* and $[C]$ and $[D]$ are molar concentration, of products C and D , respectively.

At equilibrium, the rate of two opposing reactions become equal.

Hence, at equilibrium,

$$\text{Rate of forward reaction} = \text{Rate of backward reaction}$$

$$\therefore K_f[A][B] = K_b[C][D]$$

$$\text{or } \frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

Since K_f and K_b are constants, therefore, the ratio of K_f/K_b is also constant and is represented by K_c .

$$\therefore K_c = \frac{K_f}{K_b} = \frac{[C][D]}{[A][B]} \quad \dots(i)$$

The constant K_c is called the equilibrium constant. The subscript 'c' indicates that K_c is expressed in concentration of mol L^{-1} .

The equilibrium constant for a general reaction



is expressed as

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots(ii)$$

where, $[a]$, $[b]$, $[c]$ and $[d]$ are the equilibrium concentrations of the reactants and products

Equation (i) and (ii) are the expression for the law of chemical equilibrium. It may be stated as:

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the

product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the equilibrium law or law of chemical equilibrium.

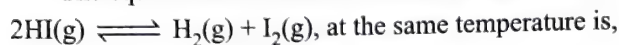
7.4.2 STOICHIOMETRIC REPRESENTATION OF EQUILIBRIUM CONSTANT

Let us write equilibrium constant for the reaction



$$\text{as, } K_c = [\text{HI}]^2 / [\text{H}_2][\text{I}_2] = x$$

The equilibrium constant for the reverse reaction,

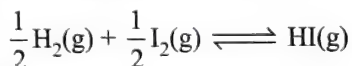


$$K'_c = [\text{H}_2][\text{I}_2] / [\text{HI}]^2 = 1/x = 1/K_c$$

$$\text{Thus, } K'_c = 1/K_c$$

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

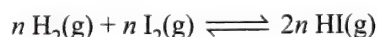
If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor, then we must make sure that the expression for equilibrium constant also reflects that change. For example, if equation (i) is written as



the equilibrium constant for the above reaction is given by

$$K''_c = [\text{HI}] / [\text{H}_2]^{1/2} [\text{I}_2]^{1/2} = \{[\text{HI}]^2 / [\text{H}_2][\text{I}_2]\}^{1/2} \\ = x^{1/2} = K_c^{1/2}$$

On multiplying equation (i) by n , we get



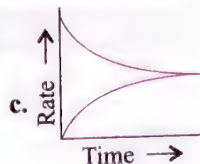
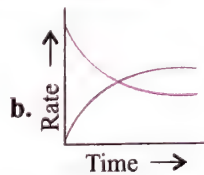
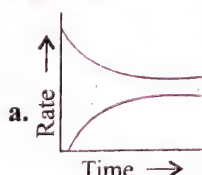
Therefore, the equilibrium constant for the reaction is equal to K_c^n . These findings are summarised in Table 7.2. It should be noted that because the equilibrium constants K_c and K'_c have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

Table 7.2 Relation between equilibrium constants for a general reaction and its multiples

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K'_c = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K''_c = (K_c^n)$

ILLUSTRATION 7.1

Which graph will show equilibrium condition?



d. None of these

Sol. c.

ILLUSTRATION 7.2

For $A + B \rightleftharpoons C + D$, the equilibrium constant is K_1 and for $C + D \rightleftharpoons A + B$, the equilibrium constant is K_2 . The correct relation between K_1 and K_2 is

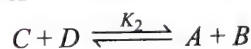
a. $K_1 \times K_2 = 1$

b. $K_1 \times (K_2 - 1) = 0$

c. $K_1/K_2 = 1$

d. All of these

Sol.



$$K_1 = \frac{1}{K_2} \Rightarrow K_1 \times K_2 = 1$$

ILLUSTRATION 7.3

For the reactions,



K_c for the reaction $A \rightleftharpoons D$ is

a. 15

b. 5

c. 3

d. 1

Sol.

a. $\frac{[B]}{[A]} = 1; \frac{[C]}{[B]} = 3; \frac{[D]}{[C]} = 5$

Multiplying all the three, $\frac{[D]}{[A]} = 1 \times 3 \times 5 = 15$

ILLUSTRATION 7.4

The law of mass action was proposed by

a. Guldberg and Waage

b. Le Chatelier and Braun

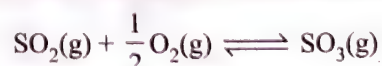
c. Kossel and Lewis

d. van't Hoff

Sol. a.

ILLUSTRATION 7.5

The equilibrium constants of the reactions



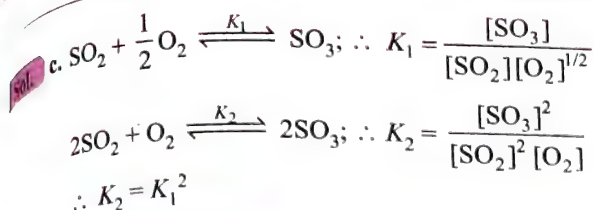
are K_1 and K_2 , respectively. The relationship between K_1 and K_2 is

a. $K_1 = K_2$

b. $K_2^2 = K_1$

c. $K_1^2 = K_2$

d. $K_2 = \sqrt{K_1}$

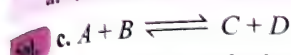
**ILLUSTRATION 7.6**

When 4 mol of A is mixed with 4 mol of B , 4 mol of C and D are formed at equilibrium, according to the reaction



the equilibrium constant is

- a. $\sqrt{2}$ b. 2 c. 1 d. 4



According to the law of mass action

$$K = \frac{[C][D]}{[A][B]} = \frac{4 \times 4}{4 \times 4} = 1$$

ILLUSTRATION 7.7

The rate at which a substance reacts, depends on its:

- a. Active mass b. Molecular mass
c. Equivalent mass d. Total volume

**ILLUSTRATION 7.8**

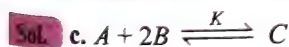
The state of equilibrium refers to

- a. State of rest b. Dynamic state
c. Stationary state d. State of inertness

**ILLUSTRATION 7.9**

For the reaction, $A + 2B \rightleftharpoons C$, the expression for equilibrium constant is

- a. $\frac{[A][B]^2}{[C]}$ b. $\frac{[A][B]}{[C]}$ c. $\frac{[C]}{[A][B]^2}$ d. $\frac{[C]}{[2B][A]}$



According to law of mass action

$$K = \frac{[C]}{[A][B]^2}$$

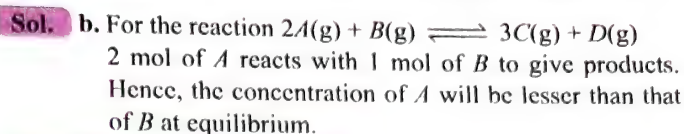
ILLUSTRATION 7.10

For the reaction:



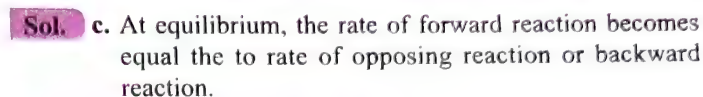
Two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium

- a. $[A] = [B]$ b. $[A] < [B]$
c. $[B] = [C]$ d. $[A] > [B]$

**ILLUSTRATION 7.11**

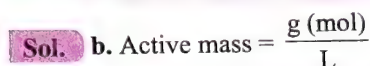
In a reversible chemical reaction, equilibrium is said to have been established when the

- a. Concentrations of reactants and products are equal
b. Opposing reactions cease
c. Speeds of opposing reactions become equal
d. Temperatures of opposing reactions are equal

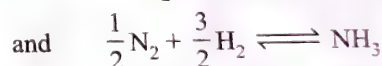
**ILLUSTRATION 7.12**

Active mass is defined as

- a. Number of g equivalent per unit volume
b. Number of g mol per L
c. Amount of substance in g per unit volume
d. Number of g mol in 100 L

**ILLUSTRATION 7.13**

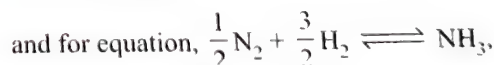
For the reactions



write down the expression for equilibrium constants K_c and K'_c . How is K_c related to K'_c ?



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \dots(i)$$



$$K'_c = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}} \quad \dots(ii)$$

Squaring equation (ii),

$$(K'_c)^2 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \dots(iii)$$

Equations (i) and (iii) are same

Thus, $K_c = (K'_c)^2$

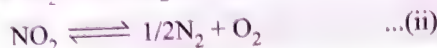
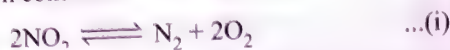
or $\sqrt{K_c} = K'_c$

ILLUSTRATION 7.14

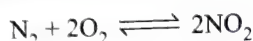
The equilibrium constant for the reaction



at a particular temperature is 100. Write down the equilibrium law equations for the following reactions and determine the values of equilibrium constants.



Sol. The equilibrium constant for the reaction



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = 100 \quad \dots(\text{a})$$

The equilibrium constant equation for reaction (i)

$$K_1 = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2} \quad \dots(\text{b})$$

This equation is reciprocal of equation (a)

$$\text{So } K_1 = \frac{1}{K_c} = \frac{1}{100} = 1 \times 10^{-2}$$

The equilibrium constant equation for reaction (ii)

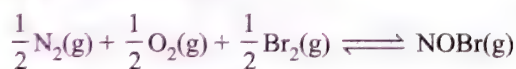
$$K_2 = \frac{[\text{N}_2]^{1/2} [\text{O}_2]}{[\text{NO}_2]} \quad \dots(\text{c})$$

Comparing equations (b) and (c),

$$K_2 = \sqrt{K_1} = \sqrt{10^{-2}} = 10^{-1} = 0.1$$

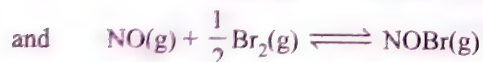
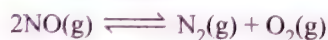
ILLUSTRATION 7.15

Determine K_c for the reaction



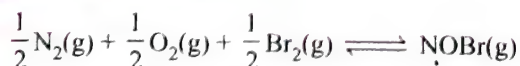
from the following data at 298 K.

The equilibrium constants for the following reactions



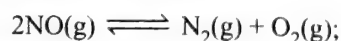
are 2.4×10^{30} and 1.4, respectively.

Sol. The net reaction is

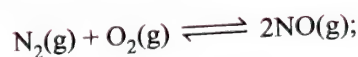


$$K_{C(\text{net})} = \frac{[\text{NOBr}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2} [\text{Br}_2]^{1/2}}$$

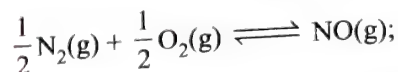
Considering the given equations:



$$\text{Equilibrium constant} = 2.4 \times 10^{30}$$

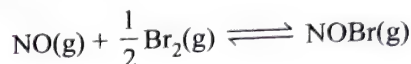


$$\text{Equilibrium constant} = \frac{1}{2.4 \times 10^{30}}$$



$$\text{Equilibrium constant} = \left(\frac{1}{2.4 \times 10^{30}} \right)^{1/2} = 0.6455 \times 10^{-15}$$

$$\frac{[\text{NO}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}} = K'_c = 0.6455 \times 10^{-15} \quad \dots(\text{i})$$



$$\frac{[\text{NOBr}]}{[\text{NO}][\text{Br}_2]^{1/2}} = K''_c = 1.4 \quad \dots(\text{ii})$$

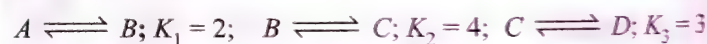
Multiplying both equations

$$\begin{aligned} \frac{[\text{NO}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}} \times \frac{[\text{NOBr}]}{[\text{NO}][\text{Br}_2]^{1/2}} \\ = K'_c \times K''_c = 0.6455 \times 10^{-15} \times 1.4 \end{aligned}$$

$$\begin{aligned} \text{or } \frac{[\text{NO}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2} [\text{Br}_2]^{1/2}} = K_{C(\text{net})} &= 0.9037 \times 10^{-15} \\ &= 9.037 \times 10^{-16} \end{aligned}$$

ILLUSTRATION 7.16

For the hypothetical reactions, the equilibrium constant (K) values are given



The equilibrium constant (K) for the reaction $A \rightleftharpoons D$ is

- a. 48 b. 6 c. 27 d. 12 e. 24

Sol. e. The reaction $A \rightleftharpoons D$ is obtained by adding the three given reactions

$$\therefore K = K_1 \times K_2 \times K_3 = 2 \times 4 \times 3 = 24$$

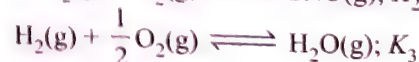
$$\text{or } K_1 = \frac{[B]}{[A]}; \quad K_2 = \frac{[C]}{[B]}; \quad K_3 = \frac{[D]}{[C]}$$

On multiplying K_1 , K_2 and K_3 , we get

$$K = K_1 \times K_2 \times K_3 = \frac{[D]}{[A]} = 24$$

ILLUSTRATION 7.17

Given:



The equilibrium constant for



will be

- a. $K_1 K_2 K_3$ b. $\frac{K_1 K_2}{K_3}$ c. $\frac{K_1 K_3^2}{K_2}$ d. $\frac{K_2 K_3^3}{K_1}$

Sol. d.

$$K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}; K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}; K_3 = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{1/2}}$$

The equilibrium constant for



will be:

$$K = \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}} = \frac{K_2 \times K_3^3}{K_1}$$

ILLUSTRATION 7.18

In a reversible reaction, study of its mechanism says that both the forward and reverse reaction follows first-order kinetics. If the half life of forward reaction ($t_{1/2f}$) is 400 s and that of reverse reaction ($t_{1/2b}$) is 250 s, the equilibrium constant of the reaction is

- a. 1.6 b. 0.433 c. 0.625 d. 1.109

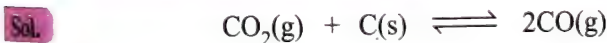
Sol. c. $t_{1/2} = \frac{0.693}{K}$ (for first-order kinetics)

$$K_f = \frac{0.693}{400} \text{ s}^{-1}; K_b = \frac{0.693}{250} \text{ s}^{-1}$$

$$K = \frac{K_f}{K_b} = \frac{250}{400} = 0.625$$

ILLUSTRATION 7.19

A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K_p if total pressure at equilibrium is 0.8 atm.



Initial	0.5 atm	0 atm
At equilibrium	(0.5 - x)	2x atm

At equilibrium, the total pressure is 0.8 atm.

$$P_{\text{total}} = P_{\text{CO}_2} + P_{\text{CO}}$$

$$0.8 = (0.5 - x) + 2x = 0.5 + x$$

$$\text{or } x = 0.3 \text{ atm}$$

Applying the law of mass action

$$K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(2 \times 0.3)^2}{0.2} = \frac{0.36}{0.2} = 1.8 \text{ atm}$$

ILLUSTRATION 7.20

A sample of $\text{CaCO}_3(\text{s})$ is introduced into a sealed container of volume 0.654 L and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction



is 3.9×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.



$$K_p = P_{\text{CO}_2} = 3.9 \times 10^{-2}$$

Let the number of moles of CO_2 be formed = n

$$n = \frac{P_{\text{CO}_2} \times V}{RT} = \frac{3.9 \times 10^{-2} \times 0.654}{0.082 \times 1000} = 3.11 \times 10^{-4} \text{ mol}$$

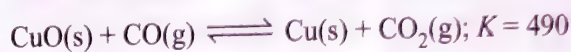
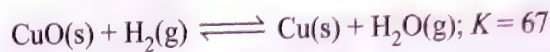
The amount of $\text{CaO}(\text{s})$ formed will also be

$$= 3.11 \times 10^{-4} \text{ mol}$$

$$\text{Hence, the mass of CaO formed} = 3.11 \times 10^{-4} \times 56 = 0.0174 \text{ g}$$

ILLUSTRATION 7.21

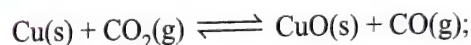
From the given data of equilibrium constants of the following reactions:



Calculate the equilibrium constant of the reaction,

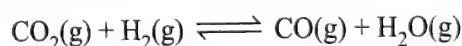


Now reversing the second reaction,



$$K_2 = \frac{1}{490}$$

Adding the two reactions, we get,



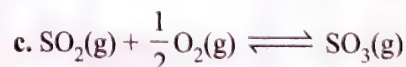
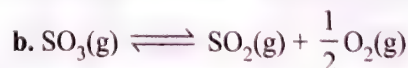
$$\text{for which } K = K_1 \cdot K_2 = 67 \times \frac{1}{490} = 0.137$$

ILLUSTRATION 7.22

Given that at 1000 K



Calculate K for the following equations:



Sol. Equation (a) is the reverse of the given equation

$$\therefore K_a = \frac{1}{261} = 0.0038 \text{ (for (a))}$$

As the equation (ii) has been obtained by dividing the equation (a) by 2, K for equation (b) will be

$$K_b = (0.0038)^2 = 0.0619$$

Reversing equation (b) we get equation (c) K for which will be

$$K = \frac{1}{0.0619} = 16.155$$

ILLUSTRATION 7.23

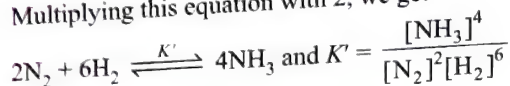
If $\text{N}_2 + 3\text{H}_2 \xrightleftharpoons{K} 2\text{NH}_3$ then $2\text{N}_2 + 6\text{H}_2 \xrightleftharpoons{K'} 4\text{NH}_3 - K'$ is equal to

- a. K^2 b. $(K)^{1/3}$ c. $1/\sqrt{K}$ d. $1/K^2$

Sol. a. For reaction $\text{N}_2 + 3\text{H}_2 \xrightleftharpoons{K} 2\text{NH}_3$;

$$\therefore K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Multiplying this equation with 2, we get



$$\text{or } K' = (K)^2$$

ILLUSTRATION 7.24

Equilibrium constants for four different reactions are given as $K_1 = 10^6$, $K_2 = 10^{-4}$, $K_3 = 10$, and $K_4 = 1$. Which reaction will take maximum time to attain equilibrium?

- a. $K_1 = 10^2$ b. $K_2 = 10^{-4}$
c. $K_3 = 10$ d. $K_4 = 20$

Sol. b. Because the minimum the value of equilibrium constant, the maximum time it will take to achieve equilibrium.

ILLUSTRATION 7.25

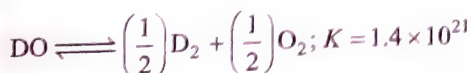
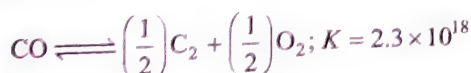
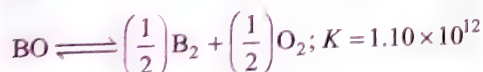
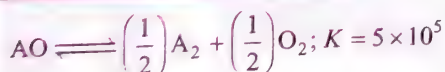
For the reactions $A \rightleftharpoons B$, $B \rightleftharpoons C$, $C \rightleftharpoons D$, equilibrium constants are K_1 , K_2 , and K_3 , respectively. What is the value of equilibrium constant for $A \rightleftharpoons D$?

- a. $K_1 + K_2 + K_3$ b. $K_1 \times K_2 \times K_3$
c. $K_1 K_2 / 3$ d. None

Sol. b. $A \xrightleftharpoons{K_1} B$, $B \xrightleftharpoons{K_2} C$, $C \xrightleftharpoons{K_3} D$

$$\therefore A \xrightleftharpoons{K_4} D \Rightarrow K_4 = K_1 \times K_2 \times K_3$$

ILLUSTRATION 7.26



Which oxide is most stable?

- a. AO b. BO c. CO d. DO

Sol. a. Because minimum the value of equilibrium constant, slower will be the reaction and hence maximum stable will be the reactant (here AO oxide)

ILLUSTRATION 7.27

Theory of 'active mass' indicates that the rate of a chemical reaction is directly proportional to the

- a. Equilibrium constant
b. Properties of reactants
c. Volume of apparatus
d. Concentration of reactants

Sol. d.

ILLUSTRATION 7.28

For a system, $A + 2B \rightleftharpoons C$, the equilibrium concentrations are $[A] = 0.06$, $[B] = 0.12$, and $[C] = 0.216$. The K_c for the reaction is

- a. 120 b. 400 c. 4×10^{-3} d. 250

Sol. d. $A + 2B \rightleftharpoons C$

$$K = \frac{[C]}{[A][B]^2} = \frac{(0.216)}{(0.06)(0.012)^2} = 250$$

ILLUSTRATION 7.29

Equilibrium constant (K) for the reaction

$2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$ is correctly given by the expression

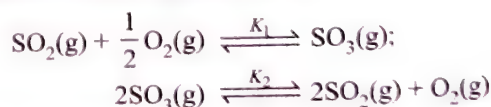
- a. $\frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]}$ b. $\frac{[2\text{NOCl}]}{[2\text{NO}][\text{Cl}_2]}$
c. $\frac{[\text{NO}]^2 + [\text{Cl}_2]}{[\text{NOCl}]}$ d. $\frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$

Sol. a. $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \xrightleftharpoons{K} 2\text{NOCl}(\text{g})$
According to the law of mass action

$$K = \frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]}$$

ILLUSTRATION 7.30

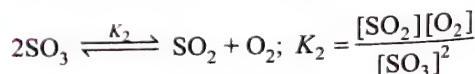
Consider the following equilibrium:



What is the relation between K_1 and K_2 ?

- a. $K_1 = \frac{1}{K_2}$ b. $K_1 = \frac{1}{\sqrt{K_2}}$
c. $K_1 = K_2$ d. $K_1 = \frac{1}{K_2^2}$

Sol. b. $\text{SO}_2 + \frac{1}{2}\text{O}_2 \xrightleftharpoons{K_1} \text{SO}_3$; $K_1 = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$

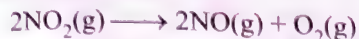


$$\text{or } \frac{K_1}{K_2} = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} \bigg/ \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

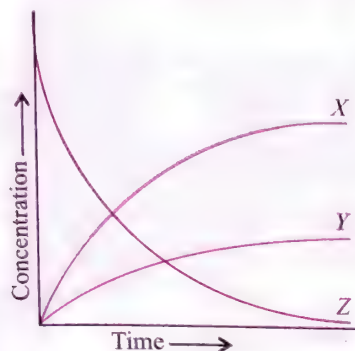
$$\text{or } K_1 = \frac{1}{\sqrt{K_2}}$$

ILLUSTRATION 7.31

Consider the following reaction:



In the figure below, identify the curves X, Y, and Z associated with the three species in the reaction



- a. $X = \text{NO}$, $Y = \text{O}_2$, $Z = \text{NO}_2$ b. $X = \text{O}_2$, $Y = \text{NO}$, $Z = \text{NO}_2$
 c. $X = \text{NO}_2$, $Y = \text{NO}$, $Z = \text{O}_2$ d. $X = \text{O}_2$, $Y = \text{NO}_2$, $Z = \text{NO}$

Sol. a. The concentration of X is increasing hence it is product, while concentration of Z decreases therefore it is reactant. The concentration of Y increases less than X that means production of Y is less than X. Hence, Y must be O_2 and X must be NO because 2 mol of NO_2 produces 2 mol of NO and 1 mol of O_2 . Therefore, $X = \text{NO}$, $Y = \text{O}_2$ and $Z = \text{NO}_2$.

ILLUSTRATION 7.32

Two equilibria $AB \rightleftharpoons A^\oplus + B^\ominus$ and $AB + B^\ominus \rightleftharpoons AB_2^\ominus$ are simultaneously maintained in a solution with equilibrium constants K_1 and K_2 , respectively. Ratio of $[A^\oplus]$ to $[AB_2^\ominus]$ in the solution is

- a. Directly proportional to $[B^\ominus]$
 b. Inversely proportional to $[B^\ominus]$
 c. Directly proportional to $[B^\ominus]^2$
 d. Inversely proportional to $[B^\ominus]^2$

Sol. d. $K_1 = \frac{[A^\oplus][B^\ominus]}{[AB]}$; $K_2 = \frac{[AB_2^\ominus]}{[AB][B^\ominus]}$
 or $[A^\oplus] = \frac{K_1[AB]}{[B^\ominus]}$, $[AB_2^\ominus] = \frac{K_2[AB][B^\ominus]}{[AB_2^\ominus]}$
 $\therefore \frac{[A^\oplus]}{[AB_2^\ominus]} \propto \frac{1}{[B^\ominus]^2}$

ILLUSTRATION 7.33

At 1400 K, $K_c = 2.5 \times 10^{-3}$ for the reaction



A 10 L reaction vessel at 1400 K contains 2.0 mol of CH_4 , 3.0 mol of CS_2 , 3.0 mol of H_2 and 4.0 mol of H_2S . In which direction does the reaction proceed to reach equilibrium?

- a. Forward b. Backward
 c. May be forward or backward
 d. Reaction is in equilibrium

Sol. b. $\text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \xrightleftharpoons{K} \text{CS}_2(\text{g}) + 4\text{H}_2(\text{g})$

$$\text{or } K = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2} \dots (i); [\text{CS}_2] = \left(\frac{3}{10}\right); [\text{H}_2] = \left(\frac{3}{10}\right);$$

$$[\text{CH}_4] = \left(\frac{2}{10}\right) \text{ and } [\text{H}_2\text{S}] = \left(\frac{4}{10}\right)$$

Substituting all the concentration values in equation (i).

$$K = \frac{\left(\frac{3}{10}\right)\left(\frac{3}{10}\right)^4}{\left(\frac{2}{10}\right)\left(\frac{4}{10}\right)^2} = \frac{3^5}{10^5} \times \frac{10^3}{2 \times 4^4} \times \frac{243}{3200} = 0.075$$

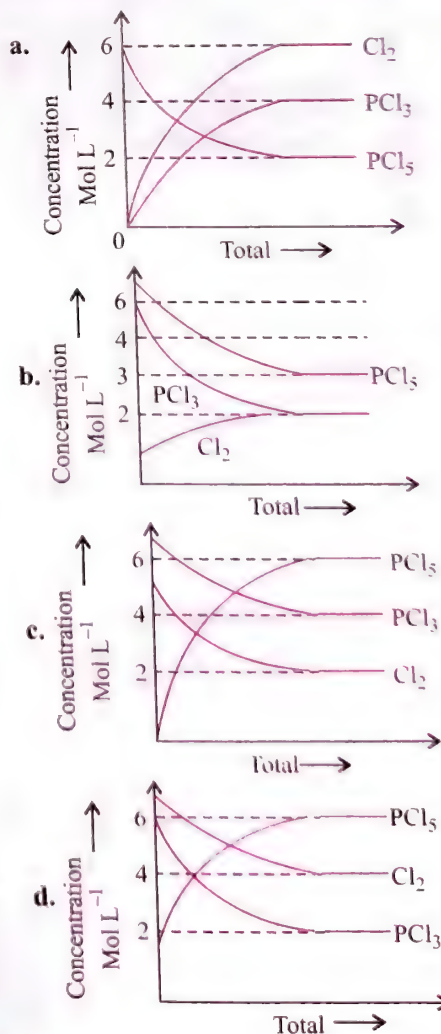
Therefore, $K > 2.5 \times 10^{-3}$ (given). Hence, the reaction will proceed in backward direction.

ILLUSTRATION 7.34

For the reaction



Which of the following sketches may represent above equilibrium? Assume equilibrium can be achieved from either side and by taking any one or more components initially. Given K_c for the reaction < 2 ?



Sol. Given:

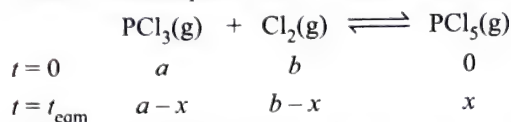
- a. From graph, find the value of K_c

$$K_c = \left(\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \right)_{\text{Eq}} = \frac{4 \times 6}{2} > 2$$

(a) is incorrect.

- b. Incorrect: Since the concentration of both $\text{PCl}_5(\text{g})$ and $\text{Cl}_2(\text{g})$ will either increase or decrease, here it is increasing for $\text{Cl}_2(\text{g})$ and decreasing for $\text{PCl}_3(\text{g})$.

- c. Note that (from graph) the initial concentration of PCl_5 is zero. So the equilibrium is established as follows:



From graph, $x = 6$. Also note that (from graph), $b < 6$ (i.e., initial concentration of Cl_2), which means that $x < 6$. It is not so, hence choice (c) is incorrect.

- d. Obviously this should be the correct choice.

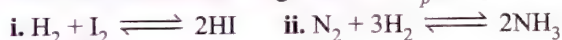
However, let us check it. Find K_c .

$$K_c = \left(\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \right)_{\text{Eqm}} = \frac{2 \times 4}{6} < 2$$

\therefore (d) is correct.

ILLUSTRATION 7.35

- a. For which of the following reactions, K_p is equal to K_c ?



- b. For which of the following cases does the reaction go farthest to completion:

$$K = 1, K = 10^{10}, K = 10^{-10}?$$

Sol.

- a. For reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ only

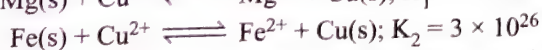
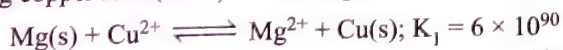
$$\Delta n = 2 - 2 = 0$$

i.e., equation (iii) reduces to $K_p = K_c$.

- b. The reaction having $K = 10^{10}$ will go farthest to completion because the ratio [product]/[reactant] is maximum in this case [Eqn. (1)].

ILLUSTRATION 7.36

Both metals Mg and Fe can reduce copper metal from a solution having copper ions (Cu^{2+}). According to the equilibria:



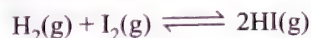
Which metal will remove cupric ion from the solution to a greater extent?

Sol.

Since $K_1 > K_2$, the product in the first reaction is much more favoured than in the second one. Mg thus removes more Cu^{2+} from solution than Fe does.

ILLUSTRATION 7.37

The equilibrium constant of the reaction



at 426°C is 55.3, what will be the value of equilibrium constant

- a. if the reaction is reversed and
b. if the given reaction is represented as

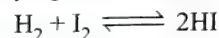
**Sol.**

- a. The reverse reaction of the given reaction is



$$\therefore \text{Equilibrium constant} = \frac{1}{55.3}$$

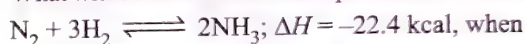
- b. The reaction $3\text{H}_2 + 3\text{I}_2 \rightleftharpoons 6\text{HI}$ has been obtained by multiplying the reaction,



by 3, hence, $K = (55.3)^3$

ILLUSTRATION 7.38

What will be the effect on the equilibrium constant for the reaction



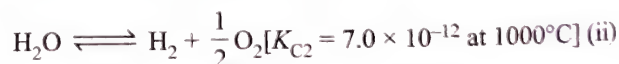
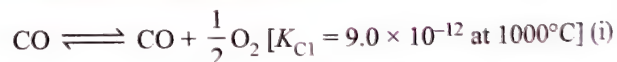
- a. Pressure is increased
b. Concentration of N_2 is increased and
c. Temperature is raised at equilibrium?

Sol.

- a. No effect } As K does not depend on
b. No effect } pressure and concentration
c. Equilibrium constant will decrease as the temperature is increased.

ILLUSTRATION 7.39

From equation (i) and (ii),



the equilibrium constant for the reaction

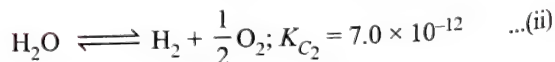
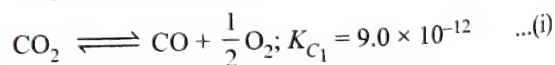


at the same temperature is

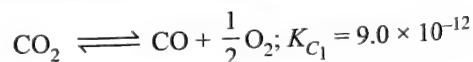
- a. 0.78 b. 2.0 c. 16.2 d. 1.28

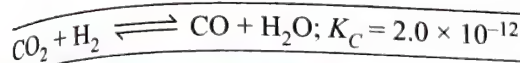
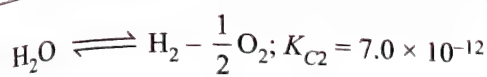
Sol.

- b. The given reactions are



Subtracting equation (ii) from (i), we get



**ILLUSTRATION 7.40**

For a reversible reaction $A + B \rightleftharpoons C$

$$\left(\frac{dx}{dt}\right) = 2.0 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1} [A][B] - 1.0 \times 10^2 \text{ s}^{-1} [C]$$

where x is the amount of 'A' dissociated. The value of equilibrium constant (K_{eq}) is

- a. 10 b. 0.05
c. 20 d. Cannot be calculated

Sol. c. $A + B \rightleftharpoons C$

$$\text{Given: } \frac{dx}{dt} = (2 \times 10^3) [A][B] - (1 \times 10^2) [C]$$

where x is the amount of 'A' dissociated.

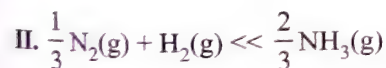
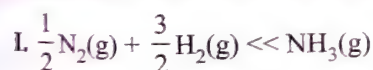
At equilibrium: $\frac{dx}{dt} = 0$ (since no change in the concentration of any reactant or product with respect to time)

$$\Rightarrow \frac{dx}{dt} = (2 \times 10^3) [A][B] - (1 \times 10^2) [C] = 0$$

$$\Rightarrow \text{Equilibrium constant } (K_{eq}) = \frac{[C]}{[A][B]} = \frac{2 \times 10^3}{1 \times 10^2} = 20$$

ILLUSTRATION 7.41

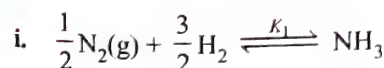
The formation of ammonia from nitrogen and hydrogen gases can be written by the following two equations:



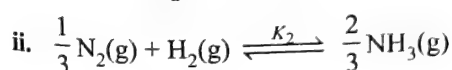
The two equations have equilibrium constants K_1 and K_2 , respectively. The relationship between the equilibrium constants is

- a. $K_1 = K_2^2$ b. $K_1^3 = K_2^2$
c. $K_1^{2/3} = K_2$ d. $K_1 = K_2^{3/2}$

Sol. c., d.



$$\therefore K_1 = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}$$



$$\therefore K_2 = \frac{[\text{NH}_3]^{2/3}}{[\text{N}_2]^{1/3} [\text{H}_2]}$$

$$\therefore K_2 = K_1^{2/3} \text{ or } K_1 = K_2^{3/2}$$

7.4.3 EQUILIBRIUM CONSTANT IN GASEOUS SYSTEMS

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products and used symbol K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as

$$PV = nRT$$

$$\Rightarrow P = \frac{n}{V} RT$$

Here, P is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 , and T is the temperature in Kelvin

Therefore, n/V is the concentration expressed in mol m^{-3} .

If concentration c is in mol L^{-1} or mol dm^{-3} and P is in bar, then

$$P = cRT,$$

We can also write $P = [\text{gas}]RT$.

Here, $R = 0.0831 \text{ bar L mol}^{-1} \text{ K}^{-1}$

At constant temperature, the pressure of the gas is proportional to its concentration, i.e.

$$P \propto [\text{gas}]$$

For reaction in equilibrium



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\text{or } K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

The equilibrium constant, K_p defined in terms of partial pressure is not the same as the equilibrium constant K_c , defined in terms of concentration.

Equilibrium constant in terms of mole fraction

When the amount of reactants and products is expressed in mole fraction, we get a new equilibrium constant and is expressed as: K_x

Consider a general reaction in equilibrium



The amount of reactants and products in mole fraction is given as:

The amount of $A = \chi_A$ (mole fraction of A)

The amount of $B = \chi_B$ (mole fraction of B)

The amount of $C = \chi_C$ (mole fraction of C)

The amount of $D = \chi_D$ (mole fraction of D)

$$\therefore \text{The equilibrium constant } K_x = \frac{(\chi_C)^c (\chi_D)^d}{(\chi_A)^a (\chi_B)^b}$$

7.4.4 RELATIONSHIP BETWEEN K_p , K_c AND K_χ

Relation between K_p and K_χ

In an ideal gaseous mixture, each component obeys Dalton's law of partial pressures, i.e., $p_i = \chi_i P$, where P is the total pressure and P_i is the partial pressure of the i th component with mole fraction χ_i in the mixture. Consider a general reaction in equilibrium.



We have, partial pressure of A; $p_A = \chi_A P$

Partial pressure of B; $p_B = \chi_B P$

Partial pressure of C; $p_C = \chi_C P$

Partial pressure of D; $p_D = \chi_D P$

$$\begin{aligned} \therefore K_p &= \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} = \left(\frac{(\chi_C)^c (\chi_D)^d}{(\chi_A)^a (\chi_B)^b} \right) P^{(c+d)-(a+b)} \\ &= K_\chi P^{\Delta n}, \end{aligned}$$

where $\Delta n = (\text{Sum of exponents in products})$

$-(\text{Sum of exponents in reactants})$

7.4.5 RELATION BETWEEN K_p AND K_c

Similarly for a general reaction



For an ideal gas,

$$PV = nRT$$

$$P = \frac{n}{V} RT = cRT$$

$$\therefore p_A = c_A RT$$

$$p_B = c_B RT$$

$$p_C = c_C RT$$

$$p_D = c_D RT$$

$$\begin{aligned} K_p &= \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} = \frac{[C]^c [D]^d (RT)^{(c+d)}}{[A]^a [B]^b (RT)^{(a+b)}} \\ &= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)} \\ &= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n} \end{aligned}$$

where $\Delta n = (\text{number of moles of gaseous products}) - (\text{number of moles of gaseous reactants})$ in the balanced chemical equation.

(It is necessary that while calculating the value of K_p , pressure should be expressed in bar as standard state is 1 bar). We have known from Unit 1.

$$1 \text{ Pa} = 1 \text{ N m}^{-2}, \text{ and } 1 \text{ bar} = 10^5 \text{ Pa}$$

K_p values for a few selected reactions at different temperatures are given in Table 7.3.

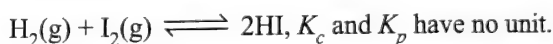
Table 7.3 Equilibrium Constants, K_p for a few selected reactions

Reaction	Temperature (K)	K_p
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	298	4.0×10^{24}
	500	2.5×10^{10}
	700	3.0×10^4
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	298	0.98
	400	47.9
	500	1700

7.4.6 UNITS OF EQUILIBRIUM CONSTANT

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol L^{-1} and for K_p partial pressure is substituted in Pa, kPa, bar, or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of the numerator and denominator are same.

For the reactions



$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, K_c has unit mol L^{-1} and K_p has unit bar.

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products is specified. For a pure gas, the standard state is 1 bar. Therefore, a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number. Standard state (c_0) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system, both K_p and K_c are dimensionless quantities but have different numerical values due to different standard states.

7.4.7 CHARACTERISTICS OF EQUILIBRIUM CONSTANT

- The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.
- If the reaction is reversed, the value of the equilibrium constant is inverted.
- If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e. \sqrt{K}).
- If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K^2).

e. If the equation (having equilibrium constant K) is written in two steps (having equilibrium constant K_1 and K_2), then $K_1 \times K_2 = K$.

Variation of equilibrium constant with variation of the reaction equation (K = equilibrium constant for original reaction) is given as below:

When the equation the new equilibrium is constant is	
Reversed	$1/K$
Divided by 2	\sqrt{K}
Multiplied by 2	K^2
Divided into two steps	$K = K_1 \times K_2$

f. The magnitude of the equilibrium constant gives an idea of the relative amounts of the reactants and the products.

g. The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.

This is because the catalyst increases the speed of the forward reaction and the backward reaction to be same extent.

ILLUSTRATION 7.42

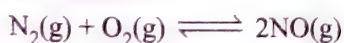
The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500 K. $[\text{N}_2] = 1.5 \times 10^{-2}$ M, $[\text{H}_2] = 3.0 \times 10^{-2}$ M, and $[\text{NH}_3] = 1.2 \times 10^{-2}$ M. Calculate the equilibrium constant.

Sol. The equilibrium constant for the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ can be written as

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = \frac{(1.2 \times 10^{-2})^2}{(1.5 \times 10^{-2})(3.0 \times 10^{-2})^3} = 0.106 \times 10^4 = 1.06 \times 10^3$$

ILLUSTRATION 7.43

At equilibrium, the concentrations of $\text{N}_2 = 3.0 \times 10^{-3}$ M, $\text{O}_2 = 4.2 \times 10^{-3}$ M, and $\text{NO} = 2.8 \times 10^{-3}$ M in a sealed vessel at 800 K. What will be K_c for the reaction

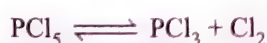


Sol. For the reaction equilibrium constant, K_c can be written as

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2.8 \times 10^{-3})^2}{(3.0 \times 10^{-3})(4.2 \times 10^{-3})} = 0.622$$

ILLUSTRATION 7.44

In the reaction, PCl_5 , PCl_3 & Cl_2 are at equilibrium at 500 K and having concentration 1.59 M PCl_3 , 1.59 M Cl_2 and 1.41 M PCl_5 . Calculate K_c for the reaction.



Sol. $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(1.59)^2}{(1.41)} = 1.79$

ILLUSTRATION 7.45

The value of K_c is 4.24 at 800 K for the reaction:



Calculate equilibrium concentrations of CO_2 , H_2 , CO and H_2O at 800 K, if only CO and H_2O are present initially at concentration of 0.10 M each.

Sol. For the reaction,



Initial concentration:

$$0.1 \text{ M} \quad 0.1 \text{ M} \quad 0 \quad 0$$

Let x M of each of the product be formed.

At equilibrium:

$$(0.1 - x) \text{ M} \quad (0.1 - x) \text{ M} \quad x \text{ M} \quad x \text{ M}$$

where x is the amount of CO_2 and H_2 at equilibrium.

$$\therefore K_c = \frac{x^2}{(0.1 - x)^2} = 4.24$$

$$x_2 = 4.24(0.01 + x^2 - 0.2x)$$

$$x^2 = 0.0424 + 4.24x^2 - 0.848x$$

$$3.24x^2 - 0.848x + 0.0424 = 0$$

$$a = 3.24, b = 0.848$$

$$c = 0.0424$$

(for quadratic equation $ax^2 + bx + c = 0$),

$$x = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$$

$$x = \frac{0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)}}{(3.24 \times 2)}$$

$$x = (0.848 \pm 0.4118)/6.48$$

$$x_1 = (0.848 - 0.4118)/6.48 = 0.067$$

$$x_2 = (0.848 + 0.4118)/6.48 = 0.194$$

The value of 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

Hence the equilibrium concentrations are,

$$[\text{CO}_2] = [\text{H}_2] = x = 0.067 \text{ M}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.1 - 0.067 = 0.033 \text{ M}$$

ILLUSTRATION 7.46

For the equilibrium,



Calculate the K_p for this reaction at this temperature

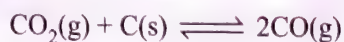
Sol. $K_p = K_c [RT]^{\Delta n}$

$$\Delta n = (2 + 1) - 2 = 1$$

$$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)^1 = 0.033$$

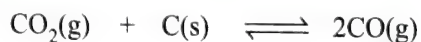
ILLUSTRATION 7.47

The value for K_p for the reaction,



is 3.0 at 1000 K. If initially $p_{\text{CO}_2} = 0.48$ bar and $p_{\text{CO}} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2

Sol. For the reaction, let 'x' be the pressure of CO_2 , then



[Initial pressure]	0.48 bar	—	0
[At equilibrium]	$(0.48 - x)$ bar	—	$2x$ bar

$$K_p = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

$$K_p = (2x)^2 / (0.48 - x) = 3.0$$

$$4x^2 - 3(0.48 - x)$$

$$4x^2 = 1.44 - 3x$$

$$4x^2 + 3x - 1.44 = 0$$

$$a = 4, b = 3, c = -1.44$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-3 \pm \sqrt{(3)^2 - 4 \times 4 \times (-1.44)}}{2 \times 4}$$

$$= (-3 + 5.66) / 8$$

(as value of x cannot be negative hence neglect that value).

$$x = 2.66 / 8 = 0.33$$

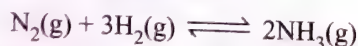
The equilibrium partial pressures are,

$$p_{\text{CO}} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

$$p_{\text{CO}_2} = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

ILLUSTRATION 7.48

40% of a mixture of 0.2 mol of N_2 and 0.6 mol of H_2 reacts to give NH_3 according to the equation:



at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases are

- a. 4:5 b. 5:4 c. 7:10 d. 8:5

Sol. a. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Moles	N_2	H_2	NH_3
Initial	0.2	0.6	0
At equilibrium	$0.2 - x$	$0.6 - 3x$	$2x$

$$\text{Also, } 0.4 = \frac{x}{0.2} \Rightarrow x = 0.08$$

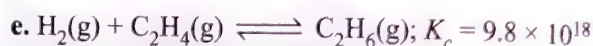
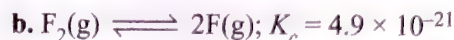
$$\text{Ratio} = \frac{V_f}{V_i} = \frac{(n_{\text{Total}})_f}{(n_{\text{Total}})_i} = \frac{0.8 - 2x}{0.8}$$

$$= 1 - \frac{x}{0.4}$$

$$= 1 - \frac{0.08}{0.40} = \frac{4}{5}$$

ILLUSTRATION 7.49

Arrange the following in order of increasing tendency of the forward reactions to proceed towards completion at 298 K and one atmospheric pressure:

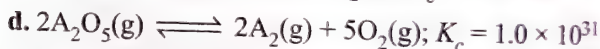
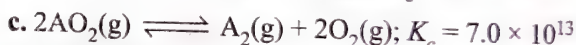
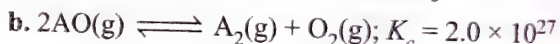
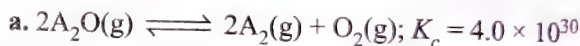


Sol. $b < d < a < e < c$

Higher the value of equilibrium constant higher is the tendency to proceed in forward direction.

ILLUSTRATION 7.50

The equilibrium constants of the dissociation of various oxides of an element A are given at constant temperature:



Write the stability of these oxides in increasing order.

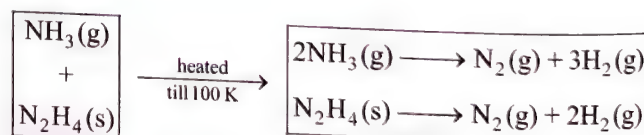
Sol. $\text{A}_2\text{O}_5 < \text{A}_2\text{O} < \text{AO} < \text{AO}_2$

At higher rate constant, the reaction will have more tendency to go on completion.

In this case, metal oxide dissociates in forward direction. Therefore, the metal oxide with lesser value of equilibrium constant will be stable.

ILLUSTRATION 7.51

At



Assuming complete decomposition of NH_3 and N_2H_4

$$P = 0.3 \text{ atm}$$

$$P = 2.7 \text{ atm}$$

$$T = 300 \text{ K}$$

$$T = 200 \text{ K}$$

$$V \text{ L}$$

$$V \text{ L}$$

Mole % of NH_3 in original mixture is (assume both concentration same volume)

- a. 25% b. 20% c. 75% d. 37.5%

c. Using equation

$$pV = nRT$$

$$n_1 = \text{moles of NH}_3$$

$$n_2 = \text{moles of N}_2\text{H}_4$$

$$0.3 \times V = (n_1 + n_2) \times R \times 300$$

$$2.7 \times V = (2n_1 + 3n_2) \times R \times 1200$$

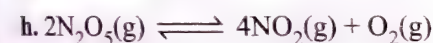
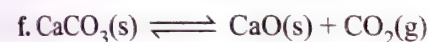
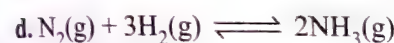
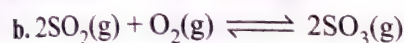
$$\frac{2n_1 + 3n_2}{n_1 + n_2} = \left(\frac{9}{4}\right)$$

$$\frac{n_1}{n_2} = \left(\frac{1}{3}\right)$$

$$\frac{n_1}{n_2} = 75\%$$

ILLUSTRATION 7.52

Write the expressions for equilibrium constant for the following reactions. If the concentrations are expressed in mol L⁻¹, give the units in each case.



Sol.

a. $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$, units; mol L

b. $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$, units; mol L⁻¹

c. $K_c = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$, units; mol L⁻¹

d. $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3}$, units; mol⁻² L²

e. $K_c = \frac{[\text{H}_2] [\text{I}_2]}{[\text{HI}]^2}$, no units

f. $K_c = [\text{CO}_2]$, units; mol L⁻¹

g. $K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$; no units

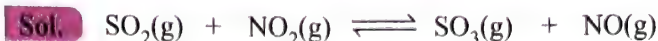
h. $K_c = \frac{[\text{NO}_2]^4 [\text{O}_2]}{[\text{N}_2\text{O}_5]^2}$; units mol³ L⁻³

ILLUSTRATION 7.53

At a certain temperature, the equilibrium constant (K_c) is 16 for the reaction:



If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO₂?



Initial	1	1	1	1
conc.				
Equilibrium	1 - x	1 - x	1 + x	1 + x
conc.				

Applying the law of mass action,

$$K_c = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\frac{1+x}{1-x} = 4 \text{ or } 1+x = 4-4x$$

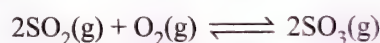
$$\text{or } 5x = 3, \text{ i.e., } x = \frac{3}{5} = 0.6$$

$$\text{Concentration of NO}_2 \text{ at equilibrium} = (1 - 0.6) = 0.4 \text{ mol}$$

$$\text{Concentration of NO at equilibrium} = (1 + 0.6) = 1.6 \text{ mol}$$

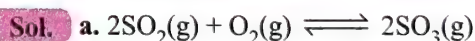
ILLUSTRATION 7.54

A mixture of SO₃, SO₂, and O₂ gases is maintained in a 10 L flask at a temperature at which the equilibrium constant for the reaction is 100:



a. If the number of moles of SO₂ and SO₃ in the flask are equal, how many moles of O₂ are present?

b. If the number of moles of SO₃ in flask is twice the number of moles of SO₂, how many moles of oxygen are present?



At equilibrium, let the number of moles of each of SO₂ and SO₃ be n_1 and of oxygen n_2 , i.e.

$$[\text{SO}_2] = \frac{n_1}{10}$$

$$[\text{O}_2] = \frac{n_2}{10}$$

$$[\text{SO}_3] = \frac{n_1}{10}$$

Applying the law of mass action,

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{\left(\frac{n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2 \left(\frac{n_2}{10}\right)} = 100$$

$$n_2 = 0.1 \text{ mol}$$

$$\text{Oxygen} = 0.1 \text{ mol}$$

b. Let the number of moles of SO₂ be = n_1

$$\text{So number of moles of SO}_3 = 2n_1$$

Let the number of moles of oxygen be = n_2

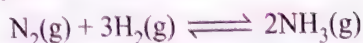
$$K_c = \frac{\left(\frac{2n_1}{100}\right)^2}{\left(\frac{n_1}{10}\right)^2 \left(\frac{n_2}{10}\right)} \text{ or } 100 = \frac{40}{n_2}$$

$$n_2 = 0.4 \text{ mol}$$

$$\text{Oxygen} = 0.4 \text{ mol}$$

ILLUSTRATION 7.55

The value of K_c for the reaction



is 0.50 at 400°C. Find the value of K_p at 400°C when concentrations are expressed in mol L⁻¹ and pressure in atm.

Sol. Applying the relationship

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = 0.50, R = 0.082 \text{ L-atm deg}^{-1} \text{ mol}^{-1}$$

$$T(400 + 273) = 673 \text{ K}, \Delta n = (2 - 4) = -2$$

$$K_p = 0.5(0.082 \times 673)^{-2} = 0.5(55.185)^{-2} = 1.64 \times 10^{-4}$$

ILLUSTRATION 7.56

For an ideal gas reaction



the value of K_p will be:

$$\text{a. } K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT^2}$$

$$\text{b. } K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT}$$

$$\text{c. } K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{RT}{V}$$

$$\text{d. } K_p = \frac{n_C n_D}{4n_A^2 n_B} \cdot \frac{V}{RT}$$

Sol. **b.** $2A + B \rightleftharpoons C + D$

$$K_p = \frac{P_C \cdot P_D}{P_A^2 \cdot P_B} = \frac{\frac{n_C RT}{V} \cdot \frac{n_D RT}{V}}{\left(\frac{n_A RT}{V}\right)^2 \cdot \left(\frac{n_B RT}{V}\right)} = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT}$$

ILLUSTRATION 7.57

For a reaction $aA(\text{g}) \rightleftharpoons bB(\text{g})$ at equilibrium, the heat of reaction at constant volume is 1500 cal more than that at constant pressure. If the temperature is 27°C, then

$$\text{a. } K_p = K_c$$

$$\text{b. } K_p > K_c$$

$$\text{c. } K_p < K_c$$

$$\text{d. None of these}$$

Sol. Since $\Delta U > \Delta H \Rightarrow \Delta n_g < 0$ [$\because \Delta H = \Delta U + \Delta n_g RT$]

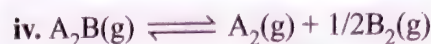
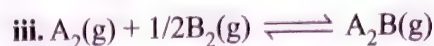
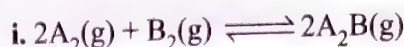
$$\text{Also, } \frac{K_p}{K_c} = (RT)^{\Delta n_g} \text{ and } RT > 1$$

$$\Rightarrow K_p < K_c$$

$$\left[\begin{array}{l} R = 0.0821 \\ T = 300 \text{ K} \end{array} \right]$$

ILLUSTRATION 7.58

Given that K_c for equation (i) given below has a value of 256 at 1000 K. Calculate the numerical values of K_c for other reactions (ii), (iii), and (iv).



Sol. ii. $\frac{1}{256}$

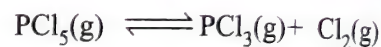
iii. 16

iv. $\frac{1}{16}$

ILLUSTRATION 7.59

At 540 K, 0.10 mol of PCl_5 is heated in a 8 L flask. The pressure of equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

Sol.



At equilibrium (mole)

$$(0.1 - x)$$

$$x$$

$$x$$

Total number of moles, $n = (0.1 - x) + x + x = (0.1 + x)$

$$PV = nRT$$

$$1 \times 8 = (0.1 + x) \times 0.082 \times 540$$

$$\text{or } x = 0.08$$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \quad \left[\begin{array}{l} [\text{PCl}_5] = \frac{0.1 - x}{V} \\ [\text{PCl}_3] = \frac{x}{V} \\ [\text{Cl}_2] = \frac{x}{V} \end{array} \right]$$

$$= \frac{x/V \times \frac{x}{V}}{(0.1 - x)/V}$$

$$= \frac{x^2}{(0.1 - x)V}$$

$$= \frac{x^2}{(0.1 - x) \times 8}$$

$$= \frac{0.08 \times 0.08}{(0.1 - 0.08)8} = 4 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_p = K_c(RT)^{\Delta n}$$

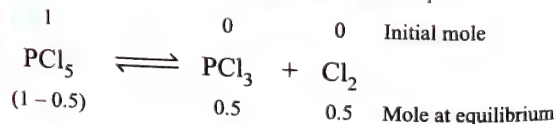
$$= K_c RT (\Delta n = +1)$$

$$= 4 \times 10^{-2} \times 0.082 \times 540 = 1.77 \text{ atm}$$

ILLUSTRATION 7.60

Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 250°C is numerically three times of K_p .

Sol.



Total mole at equilibrium = $0.5 + 0.5 + 0.5 = 1.5$

$$K_p = \frac{p_{\text{PCl}_3} \cdot p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(\frac{0.5}{1.5}P\right)\left(\frac{0.5}{1.5}P\right)}{\left(\frac{0.5}{1.5}P\right)} \quad (P \equiv \text{initial pressure})$$

$$\text{or } K_p = \frac{1}{3} \cdot P$$

$$\text{or } P = 3K_p$$

ILLUSTRATION 7.61

When sulphur in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 10% at equilibrium. This is because of conversion of some S_8 to S_2 . Find the value of equilibrium constant for this reaction.

	$S_8(g)$	\rightleftharpoons	$4S_2(g)$
Initial mole	1		0
At equilibrium	$1 - x$		$4x$
	$(1 - 0.10)$		(4×0.10)
	$= 0.9$		$= 0.40$

Applying the law of mass action,

$$K_p = \frac{[p_{S_2}]^4}{[p_{S_8}]} = \frac{(0.4)^4}{0.9} = \frac{0.0256}{0.9} \approx 0.03a$$

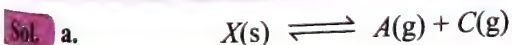
ILLUSTRATION 7.62

Two solids X and Y dissociate into gaseous products at a certain temperature as follows:



At a given temperature, the pressure over excess solid X is 40 mm and total pressure over solid Y is 80 mm. Calculate

- The values of K_p for two reactions.
- The ratio of moles of A and B in the vapour state over a mixture of X and Y .
- The total pressure of gases over a mixture of X and Y .



At equilibrium, A and C are in equal proportions, so their pressures will be same.

$$p_A = p_C$$

$$\text{Also } p_A + p_C = 40 \Rightarrow p_A = p_C = 20 \text{ mm}$$

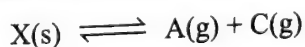
$$\Rightarrow K_p = p_A \cdot p_C = (20)^2 = 400 \text{ mm}^2$$

$$\text{Similarly for } Y(s) \rightleftharpoons B(g) + C(g),$$

$$p_B = p_C = 40 \text{ mm } (p_B + p_C = 80)$$

$$\Rightarrow K_p = p_B \cdot p_C = 40^2 = 1600 \text{ mm}^2$$

- b. Now for a mixture of X and Y , we will have to consider both the equilibrium simultaneously.



$$\text{Let } p_A = a \text{ mm}, p_B = b \text{ mm}$$

Note that the pressure of C due to dissociation of X will also be a mm and similarly the pressure of C due to dissociation of Y will also be b mm.

$$\Rightarrow p_C = (a + b) \text{ mm}$$

$$K_p \text{ (for } X) = p_A \cdot p_C = a(a + b) = 400 \quad \dots(i)$$

$$K_p \text{ (for } Y) = p_B \cdot p_C = b(a + b) = 1600 \quad \dots(ii)$$

From (i) and (ii), we get:

$$\frac{a}{b} = \frac{1}{4}$$

as volume and temperature are constant, the mole ratio will be same as the pressure ratio.

$$\begin{aligned} \text{c. The total pressure} &= P_T = p_A + p_B + p_C \\ &= a + b + (a + b) = 2(a + b) \end{aligned}$$

Adding (i) and (ii)

$$a + b = \sqrt{K_{PX} + K_{PY}} = \sqrt{2000} = 20\sqrt{5} \text{ mm}$$

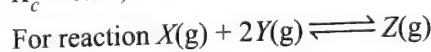
$$\Rightarrow \text{Total pressure} = 2(a + b) = 89.44 \text{ mm}$$

ILLUSTRATION 7.63

For a homogenous gaseous reaction $X(g) + 2Y(g) \rightleftharpoons Z(g)$, at 473 K, the value of $K_c = 0.35$ concentration units. When 2 moles of Y are mixed with 1 mole of X , at what pressure 60% of X is converted to Z ?

Sol. Since the pressure is to be calculated, so first find K_p using the relation between K_c and K_p .

$$K_c = 0.35, R = 0.0821, T = 473,$$



$$\Delta n_g = n_p - n_R = 1 - (2 + 1) = -2$$

$$K_p = K_c(RT)^{\Delta n} = 0.35 \times (0.0821 \times 473)^{-2} = 2.32 \times 10^{-4}$$

[Note: Volume of flask is also not given. So, convert K_c to K_p]

$$\text{The expression for } K_p \text{ is: } K_p = \frac{p_Z}{p_X(p_Y)^2}$$

Moles	X	Y	Z
Initial	1	2	0
At equilibrium	$1 - x$	$2 - 2x$	x

$$\Rightarrow \text{Total moles } (n_T) = 3 - 2x$$

Let P = equilibrium pressure, then partial pressure of X , Y and Z are:

$$\Rightarrow p_X = \frac{1-x}{3-2x}P, p_Y = \frac{2-2x}{3-2x}P, p_Z = \frac{x}{3-2x}P$$

$$K_p = \frac{\frac{x}{3-2x}P}{\left(\frac{1-x}{3-2x}P\right)\left(\frac{2-2x}{3-2x}P\right)^2} = \frac{x(3-2x)^2}{P^2(1-x)(2-2x)^2}$$

$$\Rightarrow x = 0.6 \text{ (given)}$$

$$\therefore K_p = \frac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2} = 2.32 \times 10^{-4}$$

$$\Rightarrow P^2 = (1.8 \times 10^2)^2 \Rightarrow P = 180 \text{ atm}$$

ILLUSTRATION 7.64

Solid $\text{NH}_4\text{HS(s)}$ (ammonium hydrogen sulphate) dissociates to give $\text{NH}_3(\text{g})$ and $\text{H}_2\text{S(g)}$ and is allowed to attain equilibrium at 100°C . If the value of K_p for its dissociation is found to be 0.34, find the total pressure at equilibrium and partial pressure of each component.



Since NH_4HS is a solid, hence $a_{\text{NH}_4\text{HS}} = 1$ and its undissociated amount will not effect the total pressure (due to gaseous NH_3 and H_2S only). Let x be its moles decomposed at equilibrium and P be the equilibrium pressure.

Moles	NH_4HS	NH_3	H_2S
Initial	a	0	0
At equilibrium	$a - x$	x	x

Total moles at equilibrium = Moles of $(\text{NH}_3 + \text{H}_2\text{S}) = 2x$
(only gaseous moles)

$$P = ? \quad K_p = 0.34$$

$$p_{\text{H}_2\text{S}} = \frac{x}{2x} P = \frac{P}{2} \text{ and } p_{\text{NH}_3} = \frac{x}{2x} P = \frac{P}{2}$$

(For equimolar proportions, partial pressures are equal)

$$\therefore K_p = p_{\text{H}_2\text{S}} \cdot p_{\text{NH}_3} \quad (a_{\text{NH}_4\text{HS}} = 1)$$

$$\Rightarrow 0.34 = \frac{P}{2} \times \frac{P}{2}$$

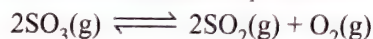
$$\Rightarrow \frac{P^2}{4} = 0.34 \Rightarrow P = \sqrt{4 \times 0.34} = 1.17 \text{ atm}$$

$$\Rightarrow p_{\text{NH}_3} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$$

$$\text{and } p_{\text{H}_2\text{S}} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$$

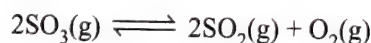
ILLUSTRATION 7.65

At 700 K, the equilibrium constant K_p for the reaction



is 1.80×10^{-3} kPa. What is the numerical value of K_c in moles per litre for this reaction at the same temperature?

Sol. For the reaction



Here $n_p = 3$ mol, $n_r = 2$ mol

$$\therefore \Delta n = n_p - n_r = 3 - 2 = 1 \text{ mole}$$

$$K_p = 1.80 \times 10^{-3} \text{ kPa}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

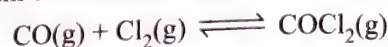
$$T = 700 \text{ K}$$

Using the relation, $K_p = K_c(RT)^{\Delta n}$

$$K_c = \frac{K_p}{RT} = \frac{1.80 \times 10^{-3}}{8.314 \times 700} = 3.09 \times 10^{-7} \text{ mol L}^{-1}$$

ILLUSTRATION 7.66

The equilibrium of formation of phosgene is represented as:

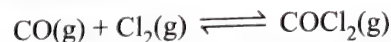


The reaction is carried out in a 500 mL flask. At equilibrium, 0.3 mol of phosgene, 0.1 mol of CO, and 0.1 mol of Cl_2 are present.

The equilibrium constant of the reaction is

- a. 30 b. 15 c. 5 d. 25

Sol. b. For the reaction



$$\text{The equation constant, } K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} \quad \dots(i)$$

$$\text{The concentration of } [\text{COCl}_2] = \frac{\text{mol}}{V(\text{L})} = \frac{0.3}{0.5} \text{ mol L}^{-1}$$

$$[\text{CO}] = \frac{0.1}{0.5} \text{ mol L}^{-1}$$

$$[\text{Cl}_2] = \frac{0.1}{0.5} \text{ mol L}^{-1}$$

Therefore, on substituting all the values in expression (i), we get

$$K_c = \frac{\frac{0.3}{0.5}}{\left(\frac{0.1}{0.5}\right)\left(\frac{0.1}{0.5}\right)} = \frac{0.3}{0.5} \times \frac{0.5}{0.1} \times \frac{0.5}{0.1} = \frac{0.15}{0.01} = 15$$

ILLUSTRATION 7.67

Which of the following relation(s) hold(s) good for gaseous and reversible reactions?

a. $\frac{K_p}{K_c} = (RT)^{(\Delta n)_g}$

b. $\frac{K_p}{K_x} = (P)^{(\Delta n)_g}$

c. $\frac{K_c}{K_x} = \left(\frac{P}{RT}\right)^{(\Delta n)_g}$

d. $\frac{K_c}{K_x} = (P)^{-(\Delta n)_g}$

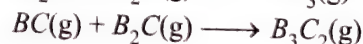
Sol. (a, b)

$$K_p = K_c(RT)^{(\Delta n)_g}$$

$$K_p = K_x(P)^{(\Delta n)_g}$$

ILLUSTRATION 7.68

If two gases AB_2 and B_2C are mixed, following equilibria are readily established:



If the reaction is started only with AB_2 with B_2C , then which of the following is necessarily true at equilibrium?

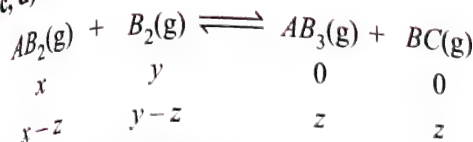
a. $[\text{AB}_3]_{\text{eq}} = [\text{BC}]_{\text{eq}}$

b. $[\text{AB}_2]_{\text{eq}} = [\text{B}_2\text{C}]_{\text{eq}}$

c. $[\text{AB}_3]_{\text{eq}} > [\text{B}_3\text{C}_2]_{\text{eq}}$

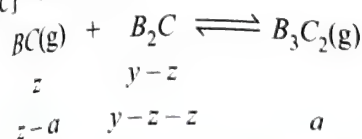
d. $[\text{AB}_3]_{\text{eq}} > [\text{BC}]_{\text{eq}}$

(c, d)



$$[AB_3] = z; [B_3C_2] = a \quad (z > a)$$

$$[BC] = z - a < z$$



CONCEPT APPLICATION EXERCISE 7.1

Objective Type

1. The equilibrium constant for the reaction



$$(1) K_c = \frac{1}{[CO_2]}$$

$$(2) K_c = [CO_2]$$

$$(3) K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$$(4) K_c = \frac{[CaCO_3]}{[CaO][CO_2]}$$

2. For the reaction
- $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$
- , the partial pressure of
- CO_2
- and
- CO
- is 2.0 and 4.0 atm, respectively, at equilibrium. The
- K_p
- of the reaction is

$$(1) 0.5 \quad (2) 5.0 \quad (3) 30.0 \quad (4) 8.0$$

3. In a chemical equilibrium,
- $K_c = K_p$
- when

(1) The number of molecules entering into a reaction is more than the number of molecules produced.

(2) The number of molecules entering into the reaction is equal to the number of molecules produced.

(3) the number of molecules entering into the reaction is less to the number of molecules produced.

(4) None of the above.

4. In a general reaction
- $A + B \rightleftharpoons AB$
- , which value of equilibrium constant most favours the production of
- AB
- ?

$$(1) 9.0 \times 10^{-3}$$

$$(2) 3.0 \times 10^{-3}$$

$$(3) 9.0 \times 10^{-7}$$

$$(4) 9.0 \times 10^{-12}$$

5. During thermal dissociation of a gas, the vapour density.

(1) Remains the same

(2) Increases

(3) Decreases

(4) Increases in some cases and decreases in others

6. The vapour density of fully dissociated
- NH_4Cl
- would be

(1) Less than half of the vapour density of pure NH_4Cl (2) Double of the vapour density of pure NH_4Cl (3) Half of the vapour density of pure NH_4Cl (4) One-third of the vapour density of pure NH_4Cl

7. In the reversible reaction,
- $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
- ,
- K_p
- is

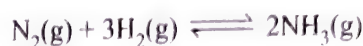
(1) Greater than K_c (2) Less than K_c (3) Equal to K_c

(4) Zero

8. At 500 K, the equilibrium constant for reaction
- $cis-C_2H_2Cl_2 \rightleftharpoons trans-C_2H_2Cl_2$
- is 0.6. At the same temperature, the equilibrium constant for the reaction
- $trans-C_2H_2Cl_2 \rightleftharpoons cis-C_2H_2Cl_2$
- will be

$$(1) 1.67 \quad (2) 1.65 \quad (3) 1.06 \quad (4) 1.60$$

9. 2 mol of
- N_2
- is mixed with 6 mol of
- H_2
- in a closed vessel of one litre capacity. If 50%
- N_2
- is converted into
- NH_3
- at equilibrium, the value of
- K_p
- for the reaction



$$(1) 4/27 \quad (2) 27/4 \quad (3) 2/27 \quad (4) 20$$

10. For the reaction,
- $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$
- , if the initial concentration of
- $[H_2] = [CO_2]$
- and
- $x \text{ mol L}^{-1}$
- of
- H_2
- is consumed at equilibrium, the correct expression of
- K_p
- is:

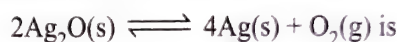
$$(1) \frac{x^2}{(1-x)^2}$$

$$(2) \frac{(1+x)^2}{(1-x)^2}$$

$$(3) \frac{1+x^2}{(2+x)^2}$$

$$(4) \frac{x^2}{1+x^2}$$

11. Partial pressure of
- O_2
- in the reaction

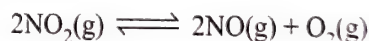


$$(1) K_p \quad (2) \sqrt{K_p} \quad (3) \sqrt[3]{K_p} \quad (4) (K_p)^2$$

12. Two moles of
- PCl_5
- is heated in a closed vessel of 2 L capacity. When the equilibrium is attained, 40% of it has been found to be dissociated. What is the value of
- K_c
- in
- mol dm^{-3}
- ?

$$(1) 0.530 \quad (2) 0.266 \quad (3) 0.130 \quad (4) 0.170$$

13. For the reaction:



$$K_c = 1.8 \times 10^{-6} \text{ at } 184^\circ\text{C}$$

$$R = 0.0831 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

when K_p and K_c are compared at 184°C , it is found that(1) K_p is greater than K_c (2) K_p is less than K_c (3) $K_p = K_c$ (4) None of the above

- 14.
- $NH_4COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
- . If equilibrium pressure is 3 atm for the above reaction,
- K_p
- will be

$$(1) 4 \quad (2) 20 \quad (3) 25 \quad (4) 15$$

- 15.
- $A + B \rightleftharpoons C + D$

If initially the concentration of A and B are both equal but at equilibrium concentration of D will be twice that of A , then what will be the equilibrium constant of the reaction?

$$(1) 1 \quad (2) 2 \quad (3) 3 \quad (4) 4$$

16. 15 mol of
- H_2
- and 5.2 moles of
- I_2
- are mixed and allowed to attain equilibrium at
- 500°C
- . At equilibrium, the concentration of
- HI
- is found to be 10 mol. The equilibrium constant for the formation of
- HI
- is.

$$(1) 50 \quad (2) 25 \quad (3) 200 \quad (4) 15$$

17. For the reaction: $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$, K_c at 427°C is $3 \times 10^6 \text{ L mol}^{-1}$. The value of K_p is)

- (1) 7.5 (2) 2.5×10^{-5}
(3) 2.0×10^{-4} (4) 1.75×10^{-4}

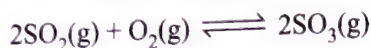
18. For the reaction



Which one is the correct representation?

- (1) $K_p = [p_{\text{H}_2\text{O}}]^2$ (2) $K_c = [\text{H}_2\text{O}]^2$
(3) $K_p = K_c(RT)^2$ (4) All

19. Which one is the correct representation for the reaction

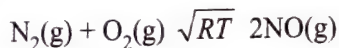


- (1) $K_p = \frac{[p_{\text{SO}_3}]^2}{[p_{\text{SO}_2}]^2 [p_{\text{O}_2}]}$
(2) $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$
(3) $K_p = \frac{[n_{\text{SO}_3}]^2}{[n_{\text{SO}_2}]^2 [n_{\text{O}_2}]} \times \left[\frac{P}{\text{Total mole}} \right]^{-1}$
(4) All the above

20. For the reaction $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)}$, K_p/K_c is equal to:

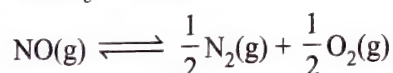
- (1) $1/RT$ (2) RT (3) \sqrt{RT} (4) $(RT)^2$

21. The equilibrium constant for the reaction



at temperature T is 4×10^{-4} .

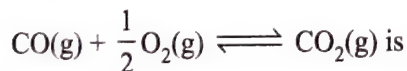
The value of K_c for the reaction



at the same temperature is

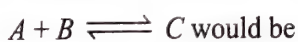
- (1) 25×10^2 (2) 50 (3) 4×10^{-4} (4) 10.00

22. K_p/K_c for the reaction



- (1) RT (2) $(RT)^{1/2}$ (3) $\frac{1}{(RT)^3}$ (4) $\frac{1}{\sqrt{RT}}$

23. The unit of equilibrium constant, K_c for the reaction



- (1) $\text{mol}^{-1} \text{L}$ (2) mol L^{-1} (3) mol L (4) No unit

24. For which of the following reactions does the equilibrium constant depend on the units of concentration?

- (1) $\text{NO(g)} \rightleftharpoons \frac{1}{2}\text{N}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$
(2) $\text{C}_2\text{H}_5\text{OH(l)} + \text{CH}_3\text{COOH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5\text{(l)} + \text{H}_2\text{O(l)}$
(3) $2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$



25. To the system,

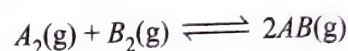
$\text{LaCl}_3\text{(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{LaClO(s)} + 2\text{HCl(g)} - \text{Heat}$
already at equilibrium, more water vapour is added without altering temperature or volume of the system. When equilibrium is re-established, the pressure of water vapour is doubled. The pressure of HCl present in the system increases by a factor of

- (1) 2 (2) $2^{1/2}$ (3) $2^{1/3}$ (4) 2^2

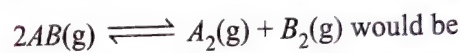
26. For the reaction, $\text{A(g)} + 2\text{B(g)} \rightleftharpoons 2\text{C(g)}$, the rate constant for forward and the reverse reactions are 1×10^{-4} and 2.5×10^{-2} respectively. The value of equilibrium constant, K for the reaction would be

- (1) 2×10^{-4} (2) 3×10^{-2} (3) 4×10^{-3} (4) 3×10^2

27. The equilibrium constant for the reaction



is 20 at 500 K. The equilibrium constant for the reaction



- (1) 20 (2) 0.5 (3) 0.05 (4) 10

28. For the reaction $\text{Ag(CN)}_2^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$, the K_c at 25°C is 4×10^{-19} . Calculate $[\text{Ag}^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in AgNO_3 .

29. At a certain temperature, the equilibrium constant K_c is 16 for the reaction, $\text{SO}_2\text{(g)} + \text{NO}_2\text{(g)} \rightleftharpoons \text{SO}_3\text{(g)} + \text{NO(g)}$. If 1.0 mol each of all the four gases is taken in a one-litre container, the concentration of NO_2 at equilibrium would be

- (1) 1.6 mol L^{-1} (2) 0.8 mol L^{-1}
(3) 0.4 mol L^{-1} (4) 0.6 mol L^{-1}

30. HI was heated in a sealed tube at 400°C till the equilibrium was reached. HI was found to be 22% decomposed. The equilibrium constant for dissociation is

- (1) 1.99 (2) 0.0199
(3) 0.0796 (4) 0.282

31. For the equilibrium $\text{AB(g)} \rightleftharpoons \text{A(g)} + \text{B(g)}$ at a given temperature, the pressure at which one-third of AB is dissociated is numerically equal to

- (1) 8 times K_p (2) 16 times K_p
(3) 4 times K_p (4) 9 times K_p

32. In a reversible reaction, if the concentration of reactants are doubled, the equilibrium constant K will:

- (1) change to $1/4 K$ (2) change to $1/2 K$
(3) change to $2 K$ (4) remain the same

33. For the equilibrium $\text{AB(g)} \rightleftharpoons \text{A(g)} + \text{B(g)}$, K_p is equal to four times the total pressure. Calculate the number moles of A formed if one mol of AB is taken initially.

- (1) 0.45 (2) 0.30 (3) 0.60 (4) 0.90

ANSWERS

Objective Type

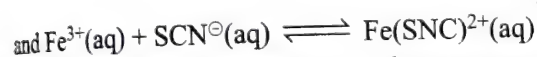
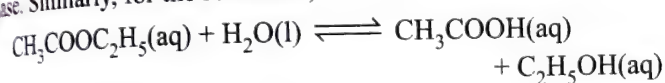
1. (2)	2. (4)	3. (2)	4. (1)	5. (3)
6. (3)	7. (3)	8. (1)	9. (1)	10. (1)
11. (1)	12. (2)	13. (1)	14. (1)	15. (4)
16. (1)	17. (4)	18. (4)	19. (4)	20. (1)
21. (2)	22. (4)	23. (1)	24. (4)	25. (2)
26. (3)	27. (3)	28. 7.5×10^{-18}		29. (3)
30. (2)	31. (1)	32. (4)	33. (4)	

7.5 TYPES OF CHEMICAL EQUILIBRIA

There are two types of chemical equilibria. These are described below.

7.5.1 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, reactants and products are in the homogeneous phase. Similarly, for the reactions,

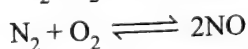


all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

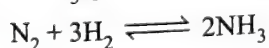
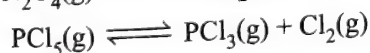
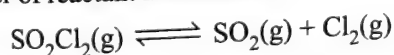
Homogeneous gaseous equilibria are best classified into two categories, i.e.

- i. In which the number of product molecules is equal to the number of reactant molecules.

For example:



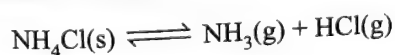
- ii. In which the number of product molecules is not equal to the number of reactant molecules,



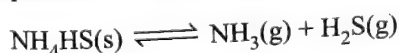
7.5.2 HETEROGENEOUS EQUILIBRIA

A chemical reaction is said to be heterogeneous if the system is having more than one phase. Few example, of heterogeneous equilibria are:

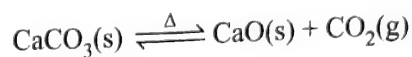
1. The dissociation of solid ammonium chloride.



2. The decomposition of solid NH_4HS .



Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words, if a substance X is involved, then $[X(s)]$ and $[X(l)]$ are constant, wherever the amount of X is taken. Contrary to this, $[X(g)]$ and $[X(aq)]$ will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.



On the basis of the stoichiometric equation, we can write

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Since $[CaCO_3(s)]$ and $[CaO(s)]$ are both constant, therefore, modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K'_c = [CO_2(g)]$$

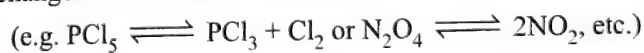
$$\text{or } K_p = p_{CO_2}$$

7.5.3 CALCULATION OF DEGREE OF DISSOCIATION FROM VAPOUR DENSITY MEASUREMENT

The degree of dissociation of a substance at a particular temperature is defined as the fraction of the total number of molecules dissociated into simpler molecules at that particular temperature, i.e.

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Number of moles dissociated}}{\text{Total number of moles taken}}$$

The degree of dissociation can be calculated from vapour density measurements for those substances that are accompanied by change in the number of moles.



Taking the example of dissociation of PCl_5 , suppose we start with 1 mol of PCl_5 and α is its degree of dissociation at the experimental temperature. Then we have

	$PCl_5(g)$	\rightleftharpoons	$PCl_3(g)$	$+$	$Cl_2(g)$
Number of moles before dissociation	1		0		0
Number of moles after dissociation	$1 - \alpha$		α		α

Suppose the volume occupied by the vapour mole⁻¹ = V L. Then,

Before dissociation: Total number of moles = 1. Hence, total volume = V L. If D is the vapour density of PCl_5 before dissociation (called theoretical vapour density), then

$$D \propto 1/V \text{ (Density } \propto 1/\text{Volume)} \quad \dots(i)$$

After dissociation: Total number of moles

$$= (1 - \alpha) + \alpha + \alpha = 1 + \alpha$$

Total volume occupied by the reaction mixture

$$= (1 + \alpha)V_L$$

Now, if d is the density of the vapour (called observed density), then

$$d \propto 1/(1 + \alpha)V \quad \dots(\text{ii})$$

Dividing equation (i) by equation (ii), we get

$$\frac{D}{d} = \frac{1/V}{1/(1 + \alpha)V} = 1 + \alpha \text{ or } \alpha = \frac{D}{d} - 1$$

$$\text{or } \alpha = \frac{D - d}{d} \quad \dots(\text{iii})$$

As molecular weight = $2 \times$ vapour density, equation (iii) can also be written as

$$\alpha = \frac{M_t - M_0}{M_0} \quad \dots(\text{iv})$$

where M_t = theoretical (calculated) molecular weight;

M_0 = observed (experimental) molecular weight.

Alternatively, observed molecular weight can be calculated from the weight of a definite volume of the vapour at particular temperature, using the relation

$$PV = \frac{w}{M} RT \text{ or } M_0 = \frac{wRT}{PV} \text{ (as } n = w/M)$$

In case of dissociation of N_2O_4 , we can write



Number of moles before dissociation

1 0

Number of moles after dissociation

$1 - \alpha$ 2α

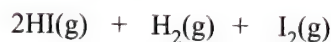
Total moles = $1 + \alpha$

Hence, the same formulae will apply as for the dissociation of PCl_5 .

ILLUSTRATION 7.69

The degree of dissociation of HI at a particular temperature is 0.8. Calculate the volume of 2 M $\text{Na}_2\text{S}_2\text{O}_3$ solution required to neutralise the iodine present in an equilibrium mixture of a reaction when 2 mol each of H_2 and I_2 are heated in a closed vessel of 2 L capacity and the equilibrium mixture is frozen.

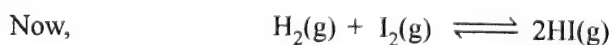
Sol.



Before dissociation 1 0 0

After dissociation $(1 - \alpha)$ $\frac{\alpha}{2}$ $\frac{\alpha}{2}$

$$\therefore K_c = \frac{\alpha^2}{4(1 - \alpha)^2} = \frac{(0.8)^2}{4(1 - 0.8)^2} = 4 \text{ (since, } \alpha = 0.8)$$



Initial moles 2 2 0

Moles after reaction $(2 - x)$ $(2 - x)$ $2x$

$$\therefore K'_c = \frac{1}{K_c} = \frac{(2x)^2}{(2 - x)^2}$$

$$\text{or } \frac{(2x)^2}{(2 - x)^2} = \frac{1}{4} \Rightarrow \frac{2x}{2 - x} = \frac{1}{2}$$

$$\text{or } x = \frac{2}{5}$$

$$\text{Thus, moles of } \text{I}_2 \text{ left} = 2 - \frac{2}{5} = \frac{8}{5}$$

Equivalents of $\text{Na}_2\text{S}_2\text{O}_3$ = Equivalents of I_2 left at equilibrium (where V is the volume in L)

$$2 \times V = \frac{8}{5} \times 2$$

$$V = 1.6 \text{ L}$$

ILLUSTRATION 7.70

At 1000 K, the pressure of iodine gas is found to be 0.1 atm due to partial dissociation of $\text{I}_2(\text{g})$ into $\text{I}(\text{g})$. Had there been no dissociation, the pressure would have been 0.07 atm. Calculate the value of K_p for the reaction: $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$.

Sol. Analysing in terms of pressure directly:

Partial pressure	I_2	I
Initial	0.07	0
At equilibrium	$0.07 - p$	$2p$

\Rightarrow Total pressure at equilibrium

$$= (0.07 - p) + 2p = 0.1 \text{ (given)}$$

$$\Rightarrow p = 0.03 \text{ atm.}$$

$$K_p = \frac{(p_{\text{I}})^2}{p_{\text{I}_2}} = \frac{(2p)^2}{(0.07 - p)} = \frac{(2 \times 0.03)^2}{0.07 - 0.03}$$

Substituting value of p , we get

$$\Rightarrow K_p = 0.09 \text{ atm units}$$

ILLUSTRATION 7.71

Calculate the percentage dissociation of $\text{H}_2\text{S}(\text{g})$ if 0.1 mol of H_2S is kept in a 0.5 L vessel at 1000 K. The value of K_c for the reaction $2\text{H}_2\text{S} \rightleftharpoons 2\text{H}_2(\text{g}) + \text{S}_2(\text{g})$ is 1.0×10^{-7} .



Volume of vessel = $V = 0.05 \text{ L}$

Let x be the degree of dissociation

Moles	H_2S	H_2	S_2
Initially	0.1	0	0
At equilibrium	$0.1 - 0.1x$	$0.1x$	$0.1x/2$

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{\left(\frac{0.1x}{V}\right)^2 \left(\frac{0.1x}{2V}\right)}{\left(\frac{0.1 - 0.1x}{V}\right)^2} = 10^{-7}$$

Assuming $0.1 - 0.1x \approx 0.1$, we get

$$\Rightarrow \frac{x^3}{2V} = 10^{-6} \Rightarrow x = 0.01$$

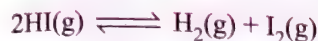
Degree of dissociation (α)

$$= \frac{\text{Amount dissociated}}{\text{Initial amount}} = \frac{0.1x}{0.1} = x$$

\Rightarrow 1% dissociation of H_2S

ILLUSTRATION 7.72

For the reaction

The degree of dissociation (α) of HI(g) is related to equilibrium constant K_p by the expression

a. $\frac{1 + 2\sqrt{K_p}}{2}$

b. $\sqrt{\frac{1 + 2K_p}{2}}$

c. $\sqrt{\frac{2K_p}{1 + 2K_p}}$

d. $\frac{2\sqrt{K_p}}{1 + 2\sqrt{K_p}}$



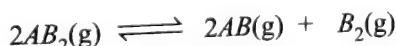
$$\begin{array}{ccc} \text{At Eq.} & 1 - \alpha & \frac{\alpha}{2} \quad \frac{\alpha}{2} \\ K_p = \frac{\left(\frac{\alpha}{2} P_T\right)^2}{(1 - \alpha)^2 P_T^2} & & \left(\because K_p = \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{(P_{\text{HI}})^2}\right) \\ \frac{\alpha}{1 - \alpha} = 2\sqrt{K_p} & & \\ \alpha = \frac{2\sqrt{K_p}}{1 + 2\sqrt{K_p}} & & \end{array}$$

ILLUSTRATION 7.73

At temperature T , a compound $\text{AB}_2(\text{g})$ dissociates according to the reaction $2\text{AB}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g}) + \text{B}_2(\text{g})$ with degree of dissociation α , which is small compared with unity. The expression for K_p in terms of α and the total pressure P_T is

a. $\frac{P_T \alpha^3}{2}$ b. $\frac{P_T \alpha^2}{3}$ c. $\frac{P_T \alpha^3}{3}$ d. $\frac{P_T \alpha^2}{2}$

Sol. c. For the given equilibrium, the equilibrium concentration are



$$\begin{array}{ccc} \text{Equilibrium} & c(1 - \alpha) & c\alpha \quad \frac{c\alpha}{2} \\ \text{concentration} & & \end{array}$$

$$\therefore K_p = \frac{(P_{\text{B}_2})(P_{\text{AB}})^2}{(P_{\text{AB}_2})^2} = \frac{\frac{c\alpha}{2} \times (c\alpha)^2 \times P_T}{[c(1 - \alpha)^2] \left[c\left(1 + \frac{\alpha}{2}\right)\right]}$$

$$K_p = \frac{\alpha^3 \times P_T}{2(1 - \alpha)^2 \left(1 + \frac{\alpha}{2}\right)}$$

Since, α is small compared to unity, so $1 - \alpha \approx 1$ and

$$1 + \frac{\alpha}{2} \approx 1.$$

$$\therefore K_p = \frac{\alpha^3 \times P_T}{2}$$

ILLUSTRATION 7.74

For the dissociation reaction

 $\text{N}_2\text{O} \rightleftharpoons 2\text{NO}_2(\text{g})$, the equilibrium constant K_p is 0.120 atm at 298 K and total pressure of system is 2 atm. Calculate the degree of dissociation of N_2O_4 .

Sol. For the reaction



At equilibrium $1 - \alpha \quad 2\alpha$

moles

Let α be the degree of dissociation and P is the total pressure, then

Total number of moles = $2\alpha + 1 - \alpha = 1 + \alpha$

$\therefore P_{\text{N}_2\text{O}} = \text{moles of } \text{N}_2\text{O} \times P_{\text{total}}$

$$= \left(\frac{1 - \alpha}{1 + \alpha}\right) P$$

and $P_{\text{NO}_2} = \left(\frac{2\alpha}{1 + \alpha}\right) P$

$$\begin{aligned} \therefore K_p &= \frac{(P_{\text{NO}_2})}{P_{\text{N}_2\text{O}}} = \frac{\left[\left(\frac{2\alpha}{1 + \alpha}\right) P\right]^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right) P} \\ &= \frac{4\alpha^2 P^2}{1 + \alpha} \times \frac{1 + \alpha}{(1 - \alpha) P} = \frac{4\alpha^2 P}{1 - \alpha^2} \quad \dots(i) \end{aligned}$$

Given $K_p = 0.120$ atm; $P = 2$ atm

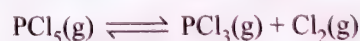
Substituting all the values in equation (i), we get

$$0.120 = \frac{4\alpha^2(2)}{(1 - \alpha^2)} = \frac{8\alpha^2}{(1 - \alpha^2)}$$

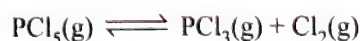
$$\Rightarrow 0.120(1 - \alpha^2) = 8\alpha^2$$

$$\therefore \text{Degree of dissociation, } \alpha = \left(\frac{0.120}{8.12}\right)^{1/2} = 0.121$$

ILLUSTRATION 7.75

 PCl_5 dissociates into PCl_3 and Cl_2 , thusIf the total pressure of the system in equilibrium is P at a density ρ and temperature T , show that the degree of dissociation $\alpha = \frac{PM}{\rho RT} - 1$, where M is the relative molar mass of PCl_5 . If thevapour density of the gas mixture at equilibrium has the value of 62 when the temperature is 230°C , what is the value of P/p ?

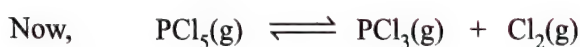
Sol. We have



Since $PV = nRT = \frac{w}{M} RT$

$$M = \frac{wRT}{PV} = \frac{\rho RT}{\rho}$$

$$\therefore V \cdot D(d) = \frac{\rho RT}{2P}$$



Initial $c \quad 0 \quad 0$

At equilibrium $c(1-\alpha) \quad c\alpha \quad c\alpha$

Total moles at equilibrium = $c(1+\alpha)$

$$\therefore \frac{\text{Total moles at equilibrium}}{\text{Total initial moles}} = \frac{\text{Initial vapour density}}{\text{Vapour density at equilibrium}}$$

$$\frac{c(1+\alpha)}{c} = \frac{D}{d}$$

$$\Rightarrow 1+\alpha = \frac{M/2}{\rho RT/2P} = \frac{PM}{\rho RT}$$

If $d = 62$ (given)

$$\frac{M}{2} = \frac{208.5}{2} = 104.25$$

$$\therefore \alpha = \frac{104.25 - 62}{62} = 0.68$$

$$\therefore \frac{P}{\rho} = \frac{(1+\alpha)RT}{M} = 0.3327 \text{ atm} / (\text{g L}^{-1})$$

ILLUSTRATION 7.76

The equilibrium constant K_p for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ at 497°C is found to be 636 mm Hg. If the pressure of the gas mixture is 182 mm, calculate the percentage dissociation of N_2O_4 . At what pressure will it be half dissociated?

Sol. For this reaction, the expression of equilibrium constant is given by:

$$K_p = \frac{4\alpha^2 P_T}{1-\alpha^2}$$

$$636 = \frac{4\alpha^2 \times 182}{1-\alpha^2} \quad \left[\because K_p = 636 \text{ (given)} \right]$$

$$P_T = 182 \text{ mm Hg}$$

$$636 - 636\alpha^2 = 728\alpha^2$$

$$1364\alpha^2 = 636$$

$$\alpha^2 = \frac{636}{1364} = 0.4663 \Rightarrow \alpha = \sqrt{0.4663} = 0.6829$$

$$\% \text{ dissociation of } \text{N}_2\text{O}_4 = 0.6829 \times 100 = 68.29$$

When the gas is half dissociated, $\alpha = 0.5$

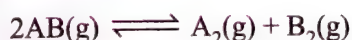
Let the pressure be P'_T mm Hg

$$\therefore 636 = \frac{4 \times (0.5)^2 \times P'_T}{1 - (0.5)^2}$$

$$P'_T = 477 \text{ mm}$$

ILLUSTRATION 7.77

For the reaction



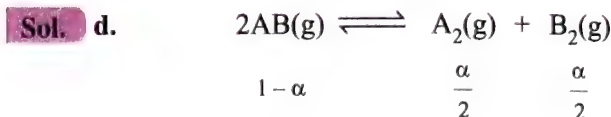
The degree of dissociation (α) of $\text{HI}(\text{g})$ is related to the equilibrium constant K_p by expression

a. $\frac{1+2\sqrt{K_p}}{2\sqrt{K_p}}$

b. $\sqrt{\frac{1+2K_p}{2}}$

c. $\sqrt{\frac{2K_p}{1+2K_p}}$

d. $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$



$$K_p = \frac{\left(\frac{\alpha}{2} \times P_T\right)^2}{(1-\alpha)^2 P_T^2}$$

$$\frac{\alpha}{1-\alpha} = 2\sqrt{K_p}$$

$$\alpha = \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

ILLUSTRATION 7.78

At a given temperature and a total pressure of 1.0 atm for the homogenous gaseous reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, the partial pressure of NO_2 is 0.5 atm.

- Find the value of K_p .
- If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture?

Sol. For equilibrium system, $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, the total pressure is 1.0 atm.

$$\Rightarrow \text{The total pressure} = p_{\text{N}_2\text{O}_4} + p_{\text{NO}_2} = 1.0$$

$$\Rightarrow p_{\text{N}_2\text{O}_4} = 0.5 \text{ atm and } p_{\text{NO}_2} = 0.5 \text{ atm}$$

a. $K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{0.5^2}{0.5} = 0.5 \text{ atm}$

According to Le Chatelier principal, when volume is decreased, the system moves in that direction where there is decrease in the number of moles. Hence, the system (here) will move in reverse direction, as there is a decrease in mole ($\Delta n_g = 2 - 1 = 1$), i.e., NO_2 will be converted to N_2O_4 .

Let the decrease in pressure of NO_2 be x atm.

Pressure	N_2O_4	NO_2
Initial	1.0	1.0
At equilibrium	$1 + x/2$	$1 - x$

- As volume is decreased to half its original volume, equilibrium is disturbed and the new initial conditions for the re-establishment of new equilibrium are:

$$p_{\text{N}_2\text{O}_4} = 1.0 \text{ atm and } p_{\text{NO}_2} = 1.0 \text{ atm}$$

$\because P$ is doubled as V is halved at constant T

$$\Rightarrow K_p = \frac{(1-x)^2}{(1+x/2)} = 0.5$$

$$\Rightarrow 4x^2 - 9x + 2 = 0$$

$$\Rightarrow x = 2 \text{ or } 0.25 \text{ (} x \neq 2, \text{ as initial pressure} = 1.0)$$

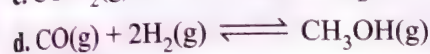
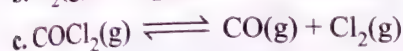
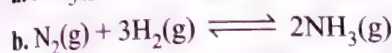
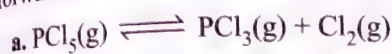
$$\Rightarrow x = 0.25$$

$$p_{\text{N}_2\text{O}_4} = 1 + \frac{x}{2} = 1.125 \text{ atm}$$

$$\text{and } p_{\text{NO}_2} = 1 - x = 0.75 \text{ atm}$$

ILLUSTRATION 7.79

In which of the following reactions, the system will shift towards the forward reaction by adding inert gas at constant pressure?



Sol. (a, c)

The equilibrium will shift in the forward direction by adding inert gas in the system where there is an increase in number of gaseous moles (i.e., $\Delta n_g > 0$) in that direction. Note that in options (a) and (c), the value of $\Delta n_g > 0$.

ILLUSTRATION 7.80

N_2O_4 dissociates as



At 40°C and one atmosphere % decomposition of N_2O_4 is 50.3%.

At what pressure and same temperature, the equilibrium mixture has the ratio of $\text{N}_2\text{O}_4 : \text{NO}_2$ as 1 : 8?

Sol. Case I $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

At Eq $(1-x) \quad 2x;$

total moles = $1+x$

$$p_{\text{N}_2\text{O}_4} = \frac{(1-x)}{(1+x)} \times P; p_{\text{NO}_2} = \frac{2x}{(1+x)} \times P$$

$$K_p = \frac{\left(\frac{2x}{1+x} \cdot P\right)^2}{\left(\frac{1-x}{1+x} \cdot P\right)} = \frac{4x^2 P}{(1-x^2)}$$

The % dissociation of N_2O_4 = 50.3% (given)

$$\text{Hence, degree of dissociation} = \frac{50.3}{100} = 0.503$$

and $P = 1$

$$\therefore K_p = \frac{4 \times (0.503)^2 \times 1}{[1 - (0.503)^2]}$$

$$\Rightarrow K_p = 1.3548 \text{ atm}$$

Case II $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$
($1-x$) $2x$

$$\text{Given, } \frac{(1-x)}{2x} = \frac{1}{8}$$

$$x = 0.8$$

Let the new pressure be P atm.

$$K_p = \frac{4x^2 P}{(1-x^2)} = \frac{4 \times 0.8 \times 0.8 \times P}{(1+0.8)(1-0.8)} = 1.3548$$

$$P = 0.19 \text{ atm}$$

ILLUSTRATION 7.81

At 627°C and 1 atm SO_3 is partially dissociated into SO_2 and O_2 by the reaction



The density of the equilibrium mixture is 0.925 g L^{-1} . What is the degree of dissociation?

Sol. Let the molecular mass of the mixture at equilibrium be M_{mix} .

Applying the relation:

$$M_{\text{mix}} = \frac{dRT}{P} = \frac{0.925 \times 0.0821 \times 900}{1} = 63.348$$

Molecular mass of $\text{SO}_3 = 80$

$$\text{Vapour density of } \text{SO}_3, D = \frac{80}{2} = 40$$

$$\text{Vapour density of mixture, } d = \frac{63.348}{2} = 34.174$$

Let the degree of dissociation be x .

$$x = \frac{D-d}{(n-1)d} = \frac{40-34.174}{\left(\frac{3}{2}-1\right) \times 34.174} = \frac{5.826 \times 2}{34.174} = 0.34$$

or $x = 34\%$ dissociated

i.e. SO_3 is 34% dissociated

ILLUSTRATION 7.82

Density of equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 384 K is 1.84 g dm^{-3} . Calculate the equilibrium constant of the reaction.



Sol. We know

$$Pm = dRT$$

$$1 \times m = 1.84 \times 0.0821 \times 384$$

$$m = 29 \times 2$$

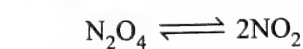
Vapour density (d) at equilibrium = 29

Initial vapour density = $M/2 = 92/2 = 46$

therefore, degree of dissociation is:

$$x = \frac{D-d}{(n-1)d} = \frac{46-29}{29} = 0.586$$

For reaction



$$t = 0 \quad 1 \quad 0$$

$$t_{\text{eq}} \quad 1-x \quad 2x$$

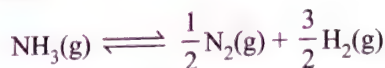
Total moles = $1+x$

$$p_{\text{N}_2\text{O}_4} = \frac{1-x}{1+x} \times P; p_{\text{NO}_2} = \frac{2x}{1+x} \times P$$

$$K_p = \frac{4x^2 P}{1-x^2} = \frac{4 \times (0.586)^2 \times 1}{1 - (0.586)^2} = 2.09 \text{ atm}$$

ILLUSTRATION 7.83

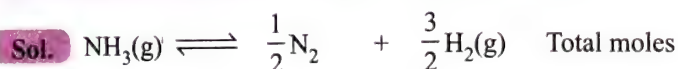
For the reaction



Show that the degree of dissociation of NH_3 is given as

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{p}{K_p} \right]^{-1/2}$$

where p is equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C , calculate K_c .



$t=0$	1	0	0	1
t_{eq}	$1-\alpha$	$\alpha/2$	$3\alpha/2$	$1+\alpha$

p_i	$\left\{ \frac{1-\alpha}{1+\alpha} \right\} p$	$\left\{ \frac{\alpha}{2(1+\alpha)} \right\} p$	$\left\{ \frac{3\alpha}{2(1+\alpha)} \right\} p$
-------	--	---	--

($p_i \rightarrow$ partial pressure)

$$K_p = \frac{(P_{\text{N}_2})^{1/2} (P_{\text{H}_2})^{3/2}}{(P_{\text{NH}_3})}$$

$$= \frac{\left[\frac{\alpha}{2(1+\alpha)} p \right]^{1/2} \left[\frac{3\alpha}{2(1+\alpha)} p \right]^{3/2}}{\left[\frac{1-\alpha}{1+\alpha} p \right]} = \frac{p\alpha^2 \sqrt{27}}{4(1-\alpha^2)}$$

Solving for α , we get $\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{p}{K_p} \right]^{-1/2}$

K_c can be calculated by using $K_p = K_c(RT)^{\Delta n}$

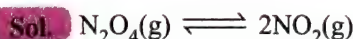
$$K_p = 78.1; T = 673; \Delta n = 1$$

$$K_c = K_p(RT)^{-1} = \frac{78.1}{(0.082 \times 673)}$$

$$K_c = \frac{78.1}{55.18} = 1.415$$

ILLUSTRATION 7.84

The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.



$$\text{Molecular mass of } \text{N}_2\text{O}_4 = (28 + 64) = 92$$

$$\text{Vapour density, } D = \frac{92}{2} = 46$$

Let the degree of dissociation be x .

$$\text{Given, } d = 30$$

Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

$$\text{Degree of dissociation} = 53.3\%$$

ILLUSTRATION 7.85

3 g mol of phosphorus pentachloride is heated in a flask of 4 L volume. At equilibrium, it dissociates to give 40% of phosphorus trichloride and chlorine. Calculate the equilibrium constant.

Sol. Degree of dissociation = 0.4



$\alpha(1-\alpha)$	$a\alpha$	$a\alpha$	(at equilibrium)
--------------------	-----------	-----------	------------------

Given, $a = 3$, $\alpha = 0.4$, and $V = 4$

So at equilibrium

$$[\text{PCl}_5] = \frac{3(1-0.4)}{4} = \frac{3 \times 0.6}{4} \text{ mol L}^{-1}$$

$$[\text{PCl}_3] = \frac{3 \times 0.4}{4} \text{ mol L}^{-1}$$

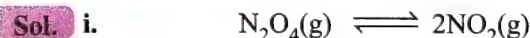
$$[\text{Cl}_2] = \frac{3 \times 0.4}{4} \text{ mol L}^{-1}$$

Applying the law of mass action,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{3 \times 0.4 \times 3 \times 0.4}{4 \times 3 \times 0.6} = 0.2 \text{ mol L}^{-1}$$

ILLUSTRATION 7.86

N_2O_4 is 25% dissociated at 37°C and 1 atm. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and 37°C .



Initial	1	0
At equilibrium	$(1-\alpha)$	2α

$$\text{Total moles} = (1-\alpha) + 2\alpha = (1+\alpha)$$

$$p_{\text{N}_2\text{O}_4} = \left(\frac{1-\alpha}{1+\alpha} \right) P, p_{\text{NO}_2} = \frac{2\alpha}{(1+\alpha)} \cdot P$$

Given, $\alpha = 0.25$ and $P = 1 \text{ atm}$

$$p_{\text{N}_2\text{O}_4} = \left(\frac{1-0.25}{1+0.25} \right) \times 1 = 0.6 \text{ atm}$$

$$p_{\text{NO}_2} = \left(\frac{2 \times 0.25}{1+0.25} \right) \times 1 = 0.4 \text{ atm}$$

$$K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ atm}$$

ii. Let the degree of dissociation of N_2O_4 at 0.1 atm be α , then

$$p_{\text{N}_2\text{O}_4} = \left(\frac{1-\alpha}{1+\alpha} \right) \times 0.1 \text{ and } p_{\text{NO}_2} = \frac{2\alpha}{(1+\alpha)} \times 0.1$$

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 \times (0.1)^2}{\left(\frac{1-\alpha}{1+\alpha}\right) \times 0.1} = \frac{4\alpha^2 \times 0.1}{(1-\alpha)(1+\alpha)} = \frac{0.4\alpha^2}{(1-\alpha^2)}$$

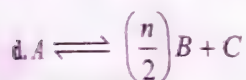
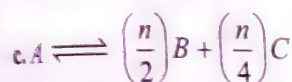
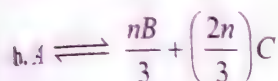
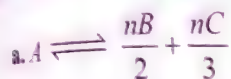
$$\text{or } 0.267 = \frac{0.4\alpha^2}{(1-\alpha^2)} \text{ or } 0.267 = 0.667\alpha^2$$

$$\alpha = 0.632$$

Hence, dissociation of $\text{N}_2\text{O}_4 = 63.2\%$

ILLUSTRATION 7.87

The equation $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for : (α is the degree of dissociation, D and d are the vapour densities before and after dissociation, respectively).



Sol. b. $\alpha = \frac{D-d}{(n-1)d} \Rightarrow (n-1)\alpha = \frac{D}{d} - 1$

$$\Rightarrow \frac{D}{d} = 1 + (n-1)\alpha$$

$$\Rightarrow \frac{d}{D} = \frac{1}{1 + (n-1)\alpha} = \frac{1}{(1-\alpha + n\alpha)}$$

\Rightarrow Any equation in which the total number of moles on product side = n and on reactant side = 1.

Clearly, (b) satisfies.

ILLUSTRATION 7.88

The vapour density of the equilibrium mixture of the reaction: $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is 50. The percent dissociation of SO_2Cl_2 is

- a. 33.00 b. 35.0 c. 30.0 d. 66.00

Sol. b. $\alpha = \frac{D-d}{(n-1)d}$

Given; $d = 50$

$$D = \frac{135}{2} = 67.5 \left(\because D = \frac{M_w}{2} \right)$$

$$\therefore \alpha = \frac{67.5 - 50}{50(2-1)} = 0.35$$

% dissociation = 35.0%

ILLUSTRATION 7.89

Consider the following equilibrium in a closed container:



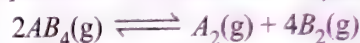
At a fixed temperature, the volume of the reaction container is halved. For this change which of the following statements holds true regarding the equilibrium constant (K_p) and the degree of dissociation (α)?

- Neither K_p nor α changes
- Both K_p and α change
- K_p does not change but α changes
- K_p changes, but α does not change

Sol. d.

ILLUSTRATION 7.90

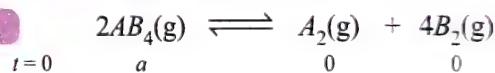
At a certain temperature T , a compound $\text{AB}_4(\text{g})$ dissociates as



with a degree of dissociation α , which is small compared to unity. The expression of K_p in terms of α and total pressure P is:

- $256P^3\alpha^5$
- $4P\alpha^2$
- $8P^3\alpha^5$
- None of these

Sol.



$$t=0 \quad \begin{array}{ccc} a & 0 & 0 \end{array}$$

(moles)

$$t=t_{\text{Eq}} \quad \begin{array}{ccc} a - a\alpha & \frac{a\alpha}{2} & 2a\alpha \end{array}$$

$$K_p = \frac{P_{\text{A}_2} \cdot P_{\text{B}_2}^4}{P_{\text{AB}_4}^2}$$

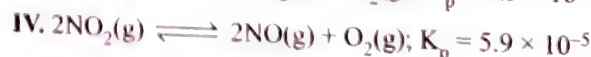
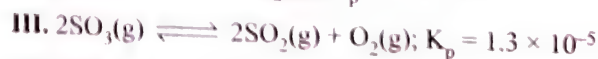
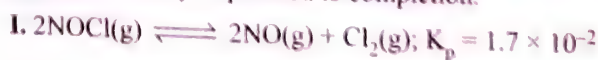
$$P_{\text{A}_2} = \frac{\frac{a\alpha}{2}}{a + \frac{3}{2}a\alpha} \cdot P \approx \frac{\alpha P}{2}; \quad P_{\text{B}_2} = \frac{\frac{2a\alpha}{3}}{a + \frac{3}{2}a\alpha} \cdot P \approx 2\alpha P$$

$$P_{\text{AB}_4} = \frac{a - a\alpha}{a + \frac{3}{2}a\alpha} \cdot P \approx P$$

$$K_p = \frac{\frac{\alpha P}{2} \cdot (2\alpha P)^4}{P^2} = 8\alpha^5 \cdot P^3$$

ILLUSTRATION 7.91

The following reaction occurs at 700 K. Arrange them in the order of increasing tendency to proceed to completion.



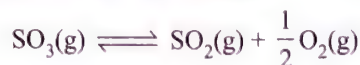
- II < I < IV < III
- III < IV < I < II
- I < III < IV < II
- IV < III < I < II

Sol. b. Higher the equilibrium constant, more will the reaction go to completion.



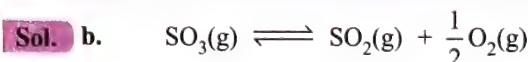
ILLUSTRATION 7.92

At 727°C and 1.2 atm of total equilibrium pressure, SO_3 is partially dissociated into SO_2 and O_2 as:



The density of equilibrium mixture is 0.9 g/L. The degree of dissociation is: [Use $R = 0.08 \text{ atm L mol}^{-1} \text{ K}^{-1}$]

- a. $\frac{1}{3}$ b. $\frac{2}{3}$ c. $\frac{1}{4}$ d. $\frac{1}{5}$



Using: $\frac{n_0}{n_{\text{mix}}} = \frac{(M_0)_{\text{mix},f}}{(M_0)_{\text{mix},i}}$... (i)

$$\text{and } PM_0 = dRT$$

$$\Rightarrow 1.2 \times M_0 = 0.9 \times 0.08 \times 1000$$

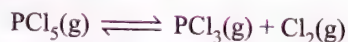
$$\Rightarrow M_0 = 60 \text{ g mol}^{-1}$$

Substituting in equation (i), we get

$$\Rightarrow \frac{1}{1+\frac{\alpha}{2}} = \frac{60}{80} \Rightarrow \alpha = 2 \left(\frac{80}{60} - 1 \right) = \frac{2}{3}$$

ILLUSTRATION 7.93

K_p for the reaction



at 250°C is 0.82. Calculate the degree of dissociation at given temperature under a total pressure of 5 atm. What will be the degree of dissociation if the equilibrium pressure is 10 atm, at same temperature.

Sol. Let 1 mol of PCl_5 be taken initially. If x moles of PCl_5 dissociate at equilibrium, its degree of dissociation = x

Moles	PCl_5	PCl_3	Cl_2
Initial	1	0	0
At equilibrium	$1-x$	x	x

$$\text{Total moles} = 1 - x + x + x = 1 + x$$

$$P = 5 \text{ atm and } K_p = 0.82$$

$$p_{\text{PCl}_5} = \left(\frac{1-x}{1+x} \right) P; p_{\text{PCl}_3} = \frac{x}{1+x} P$$

$$\text{and } p_{\text{Cl}_2} = \frac{x}{1+x} P$$

$$\text{Now, } K_p = \frac{(p_{\text{PCl}_3})(p_{\text{Cl}_2})}{(p_{\text{PCl}_5})} \Rightarrow K_p = \frac{x^2}{1-x^2} P = 0.82$$

$$\text{or } \frac{x^2(5)}{1-x^2} = 0.82 \Rightarrow x = \sqrt{\frac{0.82}{5.82}}$$

$$x = 0.375 \text{ (or 37.5\%)}$$

Now the new pressure $P = 10 \text{ atm}$.

Let y be the new degree of dissociation. As the temperature is same (250°C), the value of K_p will remain same.

Proceeding in the same manner.

$$K_p = \frac{y^2 P}{1-y^2} \Rightarrow 0.82 = \frac{y^2}{1-y^2} \times 10$$

$$\Rightarrow y = \sqrt{\frac{0.82}{10.82}} \text{ or } y = 0.275 \text{ (or 27.5\%)}$$

ILLUSTRATION 7.94

In reaction:

$\text{CH}_3\text{COCH}_3(\text{g}) \rightleftharpoons \text{CH}_3\text{CH}_3(\text{g}) + \text{CO}(\text{g})$, if the initial pressure of $\text{CH}_3\text{COCH}_3(\text{g})$ is 150 mm and at equilibrium the mole fraction of $\text{CO}(\text{g})$ is $\frac{1}{3}$, then the value K_p is

- a. 50 mm b. 100 mm c. 33.3 mm d. 75 mm

Sol.

a. 1 mol of $\text{CH}_3\text{COCH}_3 = 1 \text{ mol of } \text{CH}_3\text{CH}_3$

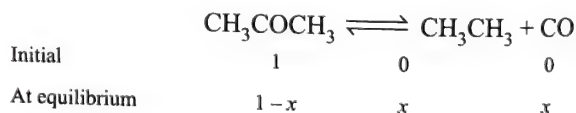
$$1 \text{ mol of CO} = \text{mole fraction of CO} = \frac{1}{3}$$

Pressure of each gas = Mole fraction \times Initial pressure

$$= \frac{1}{3} \times 150 = 50 \text{ mm}$$

$$\therefore K_p = \frac{(P_{\text{CH}_3\text{CH}_3})(P_{\text{CO}})}{(P_{\text{CH}_3\text{COCH}_3})} = \frac{50 \times 50}{50} = 50 \text{ mm}$$

Alternative method:



$$\text{Total moles} = 1 - x + x + x = 1 + x$$

$$\therefore \text{Mole fraction of CO} = \frac{x}{1+x} = \frac{1}{3} \therefore x = \frac{1}{2}$$

$$\therefore \text{Mole of each gas} = \frac{1}{2}$$

$$\therefore \text{Mole fraction of each gas} = \frac{\frac{1}{2}}{\frac{1}{2} + \frac{1}{2} + \frac{1}{2}} = \frac{1}{3}$$

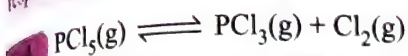
\therefore Pressure of each = Mole fraction \times Initial pressure

$$= \frac{1}{3} \times 150 = 50 \text{ mm}$$

$$\therefore K_p = \frac{(P_{\text{CH}_3\text{CH}_3})(P_{\text{CO}})}{(P_{\text{CH}_3\text{COCH}_3})} = \frac{50 \times 50}{50} = 50 \text{ mm}$$

ILLUSTRATION 7.95

When PCl_5 is heated, it dissociates into PCl_3 and Cl_2 . The vapour density of the gas mixture at 200°C and at 250°C is 70 and 58, respectively. Find the degree of dissociation at two temperatures.



Moles	PCl_5	PCl_3	Cl_2
Initial	a	0	0
At equilibrium	$a - a\alpha$	$a\alpha$	$a\alpha$

$$\text{Total moles} = a + a\alpha$$

$$\text{Using the result} = \left[\frac{d_0}{d_{\text{mix}}} = \frac{a + a\alpha}{a} \right]$$

$$d_0 = \text{density of } \text{PCl}_5$$

$$\text{At } T = 200^\circ\text{C} \quad (\text{vd} \equiv \text{vapour density})$$

$$\Rightarrow \frac{d_0}{d_{\text{mix}}} = \frac{\text{vd}_{\text{PCl}_5}}{\text{vd}_{\text{mix}}} = \frac{M_0/2}{70} = \frac{a + a\alpha}{a} = \frac{208.5/2}{70} = 1 + \alpha$$

$$\therefore \alpha = 0.49$$

$$\text{At } T = 250^\circ\text{C}$$

$$\frac{d_0}{d_{\text{mix}}} = \frac{\text{vd}_{\text{PCl}_5}}{\text{vd}_{\text{mix}}} = \frac{M_0/2}{58} = \frac{a + a\alpha}{a} = \frac{208.5/2}{58} = 1 + \alpha \Rightarrow \alpha = 0.80$$

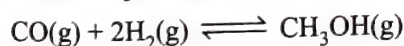
ILLUSTRATION 7.96

0.25 mol of CO taken in a 1.5 L flask is maintained at 500 K along with a catalyst so that the following reaction can take place: $\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$. Hydrogen is introduced until the total pressure of the system is 8.2 atm, at equilibrium, and 0.1 mol of methanol is formed. Calculate

a. K_p and K_c

b. The final pressure if the same amount of CO and H_2 as before are used but no catalyst so that the reaction does not take place.

Sol. a. First balance the equation as:



$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

Let y moles of H_2 were present initially.

Moles	CO	H_2	CH_3OH
Initial	0.25	y	0
At equilibrium	$0.25 - x$	$y - 2x$	x

$$x = 0.10 \text{ (given)}$$

$$\Rightarrow \text{moles of CO} = 0.25 - 0.10 = 0.15,$$

$$\text{moles of } \text{H}_2 = y - 0.2 \text{ and}$$

$$\text{moles of } \text{CH}_3\text{OH} = 0.10$$

$$\Rightarrow \text{Total moles} = n_T = 0.15 + (y - 0.2) + 0.10 = 0.05 + y$$

$$\text{Equilibrium pressure } (P) = 8.2 \text{ atm}$$

$$\text{Volume of vessel } (V) = 1.5 \text{ L}, T = 500 \text{ K}$$

Using the gas equation, $PV = nRT$, we have

$$n_T = \frac{PV}{RT} = \frac{8.2 \times 1.5}{0.0821 \times 500} = 0.3$$

$$\Rightarrow 0.30 = 0.05 + y \Rightarrow y = 0.25 \text{ moles}$$

$$\Rightarrow \text{moles of } \text{H}_2 \text{ at equilibrium} = y - 0.2 = 0.25 - 0.2 = 0.05$$

Now find K_c as follows:

$$[\text{CH}_3\text{OH}] = \frac{n}{n_T V} \text{ mol L}^{-1} = \frac{0.1}{1.5 V} \text{ mol L}^{-1}$$

$$[\text{CO}] = \frac{n}{n_T V} \text{ mol L}^{-1} = \frac{0.15}{1.5 V} \text{ mol L}^{-1}$$

$$[\text{H}_2] = \frac{n}{n_T V} \text{ mol L}^{-1} = \frac{0.15}{1.5 V} \text{ mol L}^{-1}$$

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{\frac{0.10}{1.5}}{\frac{0.15}{1.5} \left(\frac{0.05}{1.5} \right)^2} = 600$$

Now find K_p using the relation

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = 1 - 3 = -2$$

$$\Rightarrow K_p = 600 (0.0821 \times 500)^{-2} = 0.356$$

b. When no reaction takes place, then the total pressure is simply due to H_2 and CO present initially.

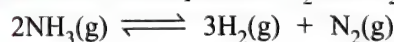
$$n_T = n_{\text{CO}} + n_{\text{H}_2} = 0.25 + 0.25 = 0.5$$

$$\Rightarrow P = \frac{nRT}{V} = \frac{0.5 \times 0.0821 \times 500}{1.5} = 13.68 \text{ atm}$$

ILLUSTRATION 7.97

Ammonia under a pressure of 15 atm, at 27°C is heated to 327°C in a closed vessel in the presence of catalyst. Under these conditions, NH_3 partially decomposes to H_2 and N_2 . The vessel is such that the volume remains effectively constant, whereas the pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed.

Sol. Ammonia decomposes to N_2 and H_2 as follows:



V remains constant

First, let us find the initial pressure of NH_3 at 327°C .

$$\Rightarrow P \propto T \text{ (V is constant)}$$

$$\Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = \frac{P_1 T_2}{T_1} = \frac{15 \times 600}{300} = 30 \text{ atm}$$

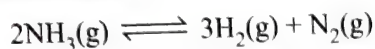
Partial pressure	NH_3	H_2	N_2
Initial	30	0	0
At equilibrium	$30 - x$	$3x/2$	$x/2$

Now final equilibrium pressure = 50 atm

$$\Rightarrow 50 = 30 - x + \frac{3}{2}x + \frac{x}{2} \Rightarrow x = 20 \text{ atm}$$

$$\Rightarrow \% \text{ NH}_3 \text{ decomposed} = \frac{20}{30} \times 100 = 66.7\%$$

Alternative method:



Let α be the degree of dissociation

Moles	NH ₃	H ₂	N ₂
Initial	a	0	0
At equilibrium	$a - a\alpha$	$3a\alpha/2$	$a\alpha/2$

$$\Rightarrow \text{Total mole} = a + a\alpha$$

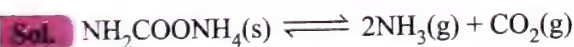
$$\frac{\text{Initial moles}}{\text{Final moles}} = \frac{\text{Initial pressure}}{\text{Final pressure}}$$

$$\frac{a}{a + a\alpha} = \frac{30}{50} \Rightarrow \alpha = \frac{20}{30}$$

$$\Rightarrow \% \text{ dissociation} = \frac{20}{30} \times 100 = 66.7\%$$

ILLUSTRATION 7.98

Solid Ammonium carbamate dissociates as: $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$. In a closed vessel, solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure. Also find the partial pressure of ammonia gas added.



Let P = original equilibrium pressure.

From the mole ratio of NH_3 and CO_2 at equilibrium, we have

$$p_{\text{NH}_3} = \frac{2}{3}P \text{ and } p_{\text{CO}_2} = \frac{P}{3}$$

$$\Rightarrow K_p = (p_{\text{NH}_3})^2 \cdot p_{\text{CO}_2} = \left(\frac{2}{3}P\right)^2 \left(\frac{P}{3}\right) = \frac{4}{27}P^3$$

Now NH_3 is added such that, $p_{\text{NH}_3} = P$

Find the pressure of CO_2

$$\Rightarrow \frac{4}{27}P^3 = P^2 \cdot p_{\text{CO}_2} \Rightarrow p_{\text{CO}_2} = \frac{4}{27}P$$

$$\text{Total new pressure} = P_{\text{new}} = p_{\text{NH}_3} + p_{\text{CO}_2}$$

$$\Rightarrow P_{\text{new}} = P + \frac{4}{27}P = \frac{31}{27}P$$

$$\Rightarrow \text{Ratio} = \frac{P_{\text{new}}}{P_{\text{original}}} = \frac{\frac{31}{27}P}{P} = \frac{31}{27}$$

Let x be the partial pressure of NH_3 added at original equilibrium.



$$\text{At equilibrium} \quad \frac{2}{3}P \quad \frac{1}{3}P$$

$$\text{When NH}_3 \text{ is added} \quad \frac{2}{3}P + x \quad \frac{1}{3}P$$

$$\text{At new equilibrium} \quad \frac{2}{3}P + x - 2y \quad \frac{1}{3}P - y$$

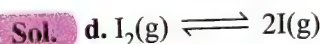
$$\Rightarrow \frac{2}{3}P + x - 2y = p_{\text{NH}_3} \text{ and } \frac{1}{3}P - y = p_{\text{CO}_2} = \frac{4}{27}P$$

$$\Rightarrow \text{Solve to get: } x = \frac{19}{27}P$$

ILLUSTRATION 7.99

The degree of dissociation of I_2 molecule at 1000°C and under 1.0 atm is 40% by volume. If the dissociation is reduced to 20% at the same temperature, the total equilibrium pressure on the gas will be:

- a. 1.57 atm b. 2.57 atm c. 3.57 atm d. 4.57 atm



Moles	I ₂	I
Initial	a	0
At equilibrium	$a - a\alpha$	$2a\alpha$

$$\Rightarrow n_T = a + a\alpha$$

$$K_p = \frac{p_{\text{I}}^2}{p_{\text{I}_2}} = \frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\frac{1-\alpha}{1+\alpha}P} = \frac{4\alpha^2 P}{(1-\alpha^2)}$$

Given: $\alpha = 0.4$ at $P = 1.0$ atm

Let P_{new} be the pressure when $\alpha = 0.2$

$$\Rightarrow K_p = \frac{4 \times 0.16}{0.84} = \frac{4 \times 0.04}{0.96} P_{\text{new}}$$

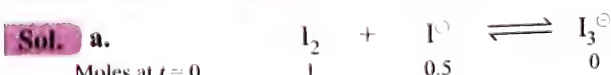
$$\Rightarrow P_{\text{new}} = \frac{4 \times 0.96}{0.84} = 4.57 \text{ atm}$$

ILLUSTRATION 7.100



This reaction is set-up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^\ominus in 1 L flask. After equilibrium is reached, excess of AgNO_3 gave 0.25 mol of yellow precipitate. Equilibrium constant is

- a. 1.33 b. 2.66 c. 2.00 d. 3.00



$$\begin{array}{ccc} \text{Moles at } t=0 & 1 & 0.5 & 0 \\ \text{Moles at } t=t_{\text{eq}} & 1-x & 0.5-x & x \end{array}$$

Excess AgNO_3 gave 0.25 mol of yellow precipitate.

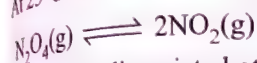


$$\Rightarrow 0.5 - x = 0.25 \Rightarrow x = 0.25$$

$$\Rightarrow K_c = \frac{[I_3^\ominus]}{[I_2][I^\ominus]} = \frac{x/V}{\left(\frac{1-x}{V}\right)\left(\frac{0.5-x}{V}\right)} = \frac{0.25/1}{\left(\frac{0.75}{1}\right)\left(\frac{0.25}{1}\right)} = 1.33 \quad (V = 1.0 \text{ L})$$

ILLUSTRATION 7.101

At 25°C and 1 atm, N_2O_4 dissociates by the reaction



If it is 35% dissociated at given condition, find the volume of above mixture will diffuse if 20 mL of pure O_2 diffuses in 10 minutes at same temperature and pressure.

Sol. For equilibrium system, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$,

Moles	N_2O_4	NO_2
Initial	a	0
At equilibrium	$a - a\alpha$	$2a\alpha$

\Rightarrow Total moles at equilibrium = $a + a\alpha$

$$p_{N_2O_4} = \frac{a - a\alpha}{a + a\alpha} P \text{ and } p_{NO_2} = \frac{2a\alpha}{a + a\alpha} P$$

Here $P = 1.0 \text{ atm}$ and $K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{4\alpha^2 P}{1 - \alpha^2} [\alpha = 0.35]$

$$\Rightarrow K_p = \frac{4 \times (0.35)^2}{1 - (0.35)^2} \times 1 = 0.56 \text{ atm}$$

$$\text{Using } \frac{a + a\alpha}{a} = \frac{M_{\text{mix}, i}}{M_{\text{mix}, f}} = \frac{M_{N_2O_4}}{M_{\text{mix}, f}}$$

$$\Rightarrow 1 + 0.35 = \frac{92}{M_{\text{mix}, f}}$$

$$\therefore M_{\text{mix}, f} = \frac{92}{1.35} = 68.15$$

Let $V(\text{mL})$ volume of mixture diffused in.

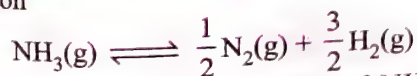
From Graham's law of diffusion

$$\frac{r_{O_2}}{r_{\text{mix}, f}} = \sqrt{\frac{M_{\text{mix}, f}}{M_{O_2}}}$$

$$\frac{20/10}{V/10} = \sqrt{\frac{68.15}{32}} \Rightarrow V = 13.70 \text{ mL}$$

ILLUSTRATION 7.102

For the reaction

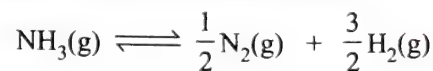


Show that the degree of dissociation of NH_3 is given as

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p} \right]^{-1/2}, \text{ where } P \text{ is the equilibrium pressure and}$$

α is the degree of dissociation. If K_p of the above reaction is 82.1 atm at 727°C, determine the value of K_c .

Sol. Let α be the degree of dissociation of $NH_3(g)$,



Initial moles	1	0	0
At equilibrium	$1 - \alpha$	$\alpha/2$	$3\alpha/2$

Total number of moles at equilibrium = $1 + \alpha$

Now,

$$p_{NH_3} = \frac{1 - \alpha}{1 + \alpha} P, p_{N_2} = \frac{\alpha/2}{1 + \alpha} P \text{ and } p_{H_2} = \frac{3\alpha/2}{1 + \alpha} P$$

$$K_p = \frac{(p_{N_2})^{1/2} (p_{H_2})^{3/2}}{p_{NH_3}}$$

$$\Rightarrow \frac{\left[\frac{\alpha}{2(1 + \alpha)} P \right]^{1/2} \left[\frac{3\alpha}{2(1 + \alpha)} P \right]^{3/2}}{\frac{1 - \alpha}{1 + \alpha} \times P} = \left[\frac{3\sqrt{3}P}{4} \right] \left[\frac{\alpha^2}{1 - \alpha^2} \right]$$

$$\Rightarrow \frac{1 - \alpha^2}{\alpha^2} = \frac{3\sqrt{3}}{4} \frac{P}{K_p}$$

$$\Rightarrow \frac{1}{\alpha^2} = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p} \right] \text{ or } \alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p} \right]^{-1/2}$$

Δn_g , change in the number of the moles of the given reaction = +1

$$K_p = K_c(RT)^{\Delta n_g} \Rightarrow K_c = K_p(RT)^{-\Delta n_g}$$

$$\Rightarrow K_c = 82.1 \times [0.0821 \times 1000]^{-1} = 1.0 \text{ mol/L}$$

7.6 EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

The value of equilibrium constant for a particular reaction depends upon the temperature. Therefore, on increasing the temperature the rate of chemical reaction also increases. However the extent of this increase in the rate of reaction depends upon the energy of activation of the reaction.

Now, since the energy of activation for the forward and backward reactions are different, so a given increase in temperature will increase the rate of the forward and backward reactions to different extents. In other words, the values of the rate constants for forward and backward reactions, i.e., k_f and k_b will change differently with a given rise or fall in temperature. Further, since $K = k_f/k_b$, therefore, the value of the equilibrium constant (K) will change.

Thus, we conclude that the equilibrium constant for a particular reaction changes with temperature. Further, it has to be noted that the value of the equilibrium constant of an endothermic reaction increases (k_f increases more than k_b) and that of an exothermic reaction decreases (k_b increases more than k_f) with rise in temperature. For reactions having zero heat of reaction, temperature has no effect on the value of K .

Quantitatively, the effect of temperature on the equilibrium constant is given by *van't Hoff equation*, viz.

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

where ΔH^\ominus is the standard enthalpy change of the reaction or in the integrated form, it may be written as (assuming ΔH^\ominus to be constant in the temperature range T_1 to T_2)

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H^\ominus}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

where $(K_p)_1$ = equilibrium constant at temperature T_1

$(K_p)_2$ = equilibrium constant at temperature T_2

ILLUSTRATION 7.103

For the formation of ammonia the equilibrium constant data at 673 K and 773 K, respectively, are 1.64×10^{-4} and 1.44×10^{-5} respectively. Calculate heat of reaction ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Sol. The given data are:

$$K_1 = 1.64 \times 10^{-4}; T_1 = 673 \text{ K}$$

$$K_2 = 1.44 \times 10^{-5}; T_2 = 773 \text{ K}$$

Using van't Hoff equation,

$$\log \left(\frac{K_p}{K_1} \right) = \frac{\Delta H}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\therefore \log \frac{1.44 \times 10^{-5}}{1.64 \times 10^{-4}} = \frac{\Delta H}{8.314 \times 2.303} \left(\frac{773 - 673}{773 \times 673} \right)$$

$$-1.0565 = \frac{\Delta H}{19.147} \left(\frac{100}{520229} \right)$$

$$\therefore \Delta H = \frac{-1.0565 \times 19.147 \times 520229}{100}$$

$$= -105216 \text{ J} = -105.216 \text{ kJ}$$

ILLUSTRATION 7.104

For the reaction



K is 0.63 at 700°C and 1.66 at 1000°C .

a. What is the average ΔH^\ominus for the temperature range considered?

b. What is the value of K at 800°C ?

Sol.

a. $T_1 = 700 + 273 = 973 \text{ K}$,

$$T_2 = 1000 + 273 = 1273 \text{ K}$$

$$K_1 = 0.63, K_2 = 1.66$$

Using the van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\ominus}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \log \left(\frac{1.66}{0.63} \right) = \frac{\Delta H^\ominus}{2.303(1.99)} \left(\frac{1273 - 973}{1273 \times 973} \right)$$

$$\Rightarrow \Delta H^\ominus = 8.0 \times 10^3 \text{ cal} = 8.0 \text{ kcal}$$

Note: The units of R and ΔH must be same.

b. Let K_2 be the equilibrium at $T_2 = 1073 \text{ K}$, $T_1 = 973 \text{ K}$, and then $K_1 = 0.63$

$$\Rightarrow \log \left(\frac{K_2}{0.63} \right) = \frac{8.0 \times 10^3}{2.303(1.99)} \left(\frac{1073 - 973}{1073 \times 973} \right)$$

$$\Rightarrow K_2 = 0.93$$

ILLUSTRATION 7.105

The value of K for the reaction



Changed from 0.096 at 298 K to 1.4 at 373 K. Above what temperature will the reaction become thermodynamically spontaneous in the forward direction assuming that ΔH^\ominus and ΔS^\ominus values for the reaction do not change with change in temperature? Given that $\Delta S^\ominus_{298} = 10.296 \text{ J K}^{-1}$.

Sol. We have

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\ominus}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{1.4}{0.096} = \frac{\Delta H^\ominus}{2.303 \times 8.314} \left(\frac{373 - 298}{373 \times 298} \right)$$

$$\Delta H^\ominus = 33025 \text{ J}$$

Now the temperature above which the forward reaction will be spontaneous is actually the temperature at which the reaction attains equilibrium, that is, when $K = 1$ or $\log K = 0$

$$\therefore \Delta G^\ominus = -2.303 RT \log K = -2.303 RT \log 1.0 = 0$$

From thermodynamics, we get

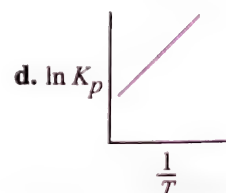
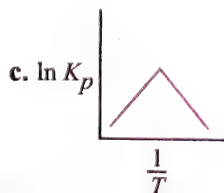
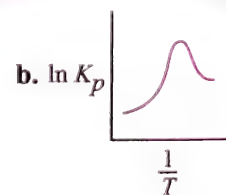
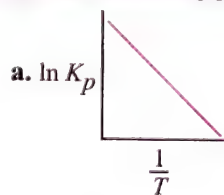
$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$

$$0 = 33025 - T \times 10.296$$

$$\text{or } T = 320.75 \text{ K}$$

ILLUSTRATION 7.106

Which of the following graph represents an exothermic reaction?



Sol. d. $\ln K_p = \ln \left(\frac{A_f}{A_r} \right) - \frac{(E_{af} - E_{ar})}{RT} = \ln \left(\frac{A_f}{A_r} \right) - \frac{\Delta H}{RT}$

For exothermic, $\Delta H = -ve$, (as $E_{af} > E_{ar}$)

$$\therefore \ln K_p = \ln \left(\frac{A_f}{A_r} \right) + \frac{\Delta H}{RT}$$

$$Y = c + mx$$

Since the slope is positive, hence the correct option is (d).

ILLUSTRATION 7.107

A reversible reaction is endothermic in forward direction. Then which of the following is(are) correct?

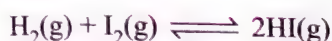
- $\ln K$ vs $1/T$ will be a straight line with negative slope
- $\frac{d}{dT} \ln K > 0$.
- A plot of $d \ln K$ against $1/T^2$ will have positive slope.
- An increase in temperature will shift the reaction in the forward direction.

Sol. (a, b, c) $K_{eq} = e^{-\Delta H/RT}$ (A, B, C)

$\Delta H > 0$ (f); $T \uparrow$; Reaction proceed in forward direction by absorbing heat.

ILLUSTRATION 7.108

The activation energy of



in equilibrium for the forward reaction is 167 kJ mol^{-1} whereas for the reverse reaction is 180 kJ mol^{-1} . The presence of catalyst lowers the activation energy by 80 kJ mol^{-1} . Assuming that the reactions are made at 27°C and the frequency factor for forward and backward reactions are 4×10^{-4} and 2×10^{-3} respectively, calculate K_c .

Sol. A catalyst lowers the activation energy for forward reaction as well as for backward reaction by equal amount.

Thus, in presence of catalyst,

Energy of activation for forward reaction

$$(E_{a1}) = 167 - 80 = 87 \text{ kJ mol}^{-1}$$

Energy of activation for backward reaction

$$(E_{a2}) = 180 - 80 = 100 \text{ kJ mol}^{-1}$$

$$\therefore \text{For forward reaction, } K_1 = A_1 e^{-E_{a1}/RT}$$

$$\text{For backward reaction, } K_2 = A_2 e^{-E_{a2}/RT}$$

where A_1 and A_2 are frequency factors and E_{a1} and E_{a2} are energies of activation after addition of catalyst.

$$\therefore K_c = \frac{K_1}{K_2} = \frac{A_1}{A_2} e^{[(-E_{a1}/RT) + (-E_{a2}/RT)]}$$

$$= \frac{A_1}{A_2} e^{\frac{[E_{a2} - E_{a1}]}{RT}} = \frac{4 \times 10^{-4}}{2 \times 10^{-3}} e^{\frac{(100 - 87)}{(8.314 \times 10^{-3} \times 300)}}$$

$$\therefore K_c = 2 \times 10^{-1} e^{[13/8.314 \times 10^{-3} \times 300]}$$

$$K_c = 36.8$$

ILLUSTRATION 7.109

Variation of K with temperature as given by van't Hoff equation can be written as

$$\text{a. } \log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\text{b. } \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\text{c. } \log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

d. None of the above

$$\text{Sol. c. } \log \frac{K_2}{K_1} = \frac{-\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

ILLUSTRATION 7.110

It is known that the heat is needed to dissociate ammonia into N_2 and H_2 . For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_f is the velocity constant for forward reaction and K_b is velocity constant for backward reaction, K_c is equilibrium constant for the reaction

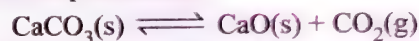
shown. Then $\frac{dk_f}{dT}$ (where T is symbol for absolute temp.):

- Is greater than dk_b/dT
- Is less than dk_b/dT
- Is equal to dk_b/dT
- Cannot be compared with dk_b/dT

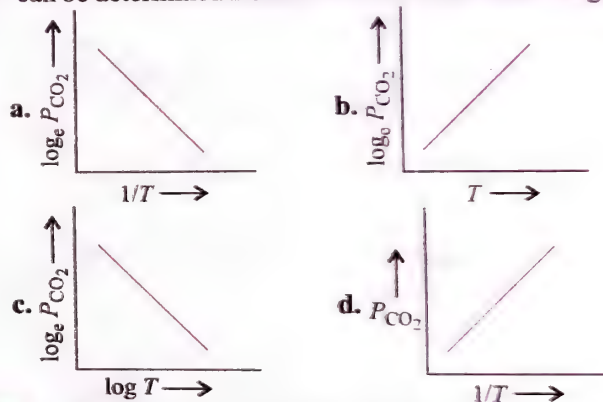
Sol. b.

ILLUSTRATION 7.111

For the chemical equilibrium,



$\Delta_r H^\circ$ can be determined from which one of the following plots?



Sol. a. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = P_{CO_2}$$

According to Arrhenius equation:

$$K = Ae^{-\Delta H^\circ_f/RT}$$

$$\log K_p = \log A - \frac{\Delta H^\circ_r}{2.303 RT}$$

$$\log P_{CO_2} = \log A - \frac{\Delta H^\circ_r}{2.303 R T} \quad \dots(i)$$

$$Y = C + MX$$

Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.

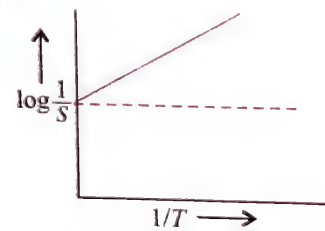
ILLUSTRATION 7.112

Solubility of a solute in water is dependent on temperature as given by $S = Ae^{-\Delta H/RT}$, where ΔH = heat of solution



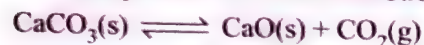
For a given solution, variation of $\log S$ with temperature is shown graphically. Hence, solute is

- $CuSO_4 \cdot 5H_2O$
- NaCl
- Sucrose
- CaO



Sol. d.**ILLUSTRATION 7.113**

In the preparation of CaO from CaCO_3 using the equilibrium,



K_p is expressed as

$$\log K_p = 7.282 - \frac{8500}{T}$$

For complete decomposition of CaCO_3 , the temperature in celsius to be used is:

- a. 1167 b. 894 c. 8500 d. 850

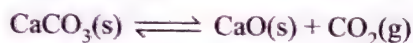
Sol. b. On complete decomposition of CaCO_3

$$\log K_p = 0$$

$$\text{therefore } \frac{8500}{T} = 7.282 \text{ or } T = \frac{8500}{7.282} = 894^\circ\text{C}$$

ILLUSTRATION 7.114

The partial pressure of CO_2 in the reaction



is 0.773 mm at 500°C . Calculate K_p at 600°C for the above reaction, ΔH of the reaction is 43.2 kcal per mole and does not change in the given range of temperature.

Sol. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$K_p = p_{\text{CO}_2}$$

Here K_p includes the constant active masses of CaCO_3 and CaO which are solids.

Thus,

$$K_{p1} = 0.773 \text{ mm at } 500^\circ\text{C}$$

$$K_{p2} = p \text{ mm (say) at } 600^\circ\text{C}$$

$$\Delta H = 43.2 \text{ kcal mol}^{-1} = 43200 \text{ cal}$$

Now we have,

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{p}{0.773} = \frac{43200}{2.303 \times 1.98} \left(\frac{873 - 773}{873 \times 773} \right)$$

$$(R = 1.98 \text{ cal deg}^{-1} \text{ mol}^{-1})$$

$$p = 19.6 \text{ mm}$$

$$\therefore K_p \text{ at } 600^\circ\text{C} \text{ is } 19.6 \text{ mm.}$$

ILLUSTRATION 7.115

For the reaction $\text{Br}_2 \rightleftharpoons 2\text{Br}$, the equilibrium constants at 327°C and 527°C are, respectively, 6.1×10^{-12} and 1.0×10^{-7} . What is the nature of the reaction?

Sol. We have

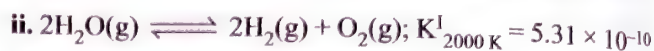
$$\log K_{p2} - \log K_{p1} = \frac{\Delta H}{2.303 R} \times \frac{T_2 - T_1}{T_2 T_1}$$

As we know from the above equation that if on increasing temperature, K_p increases, ΔH becomes positive, i.e., the

reaction is endothermic. Thus, from the given data, we see that the reaction is endothermic.

ILLUSTRATION 7.116

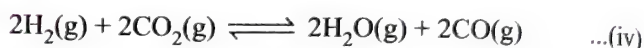
From the following data



Show whether reaction (iii) is exothermic or endothermic.

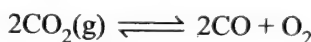
Sol. Let us consider reactions (i) and (ii)

Multiplying reaction (i) by 2, we get.



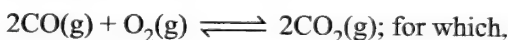
$$K_{2000\text{K}}^{\text{II}} = K_{2000\text{K}}^2 = (4.40)^2$$

Adding (iv) and (ii), we have



$$K_{2000\text{K}}^{\text{III}} = K_{2000\text{K}}^{\text{II}} \times K_{2000\text{K}}^I = (4.40)^2 \times 5.31 \times 10^{-10}$$

Therefore, by reversing the reaction, we get reaction (iii) but at 2000 K.



$$K_{2000\text{K}}^{\text{IV}} = \frac{1}{K_{2000\text{K}}^{\text{III}}} = \frac{1}{(4.40)^2 \times 5.31 \times 10^{-10}} = 9.72 \times 10^7$$

From reactions (iii) and (v), we see that as the temperature increases, the equilibrium constant decreases ($9.72 \times 10^7 < 2.24 \times 10^{22}$). Reaction (iii) is thus exothermic because ΔH will be negative.

ILLUSTRATION 7.117

The equilibrium constant K_p for the reaction,



is 1.64×10^{-4} at 400°C and 0.144×10^{-4} at 500°C . Calculate the mean heat of formation of 1 mol of NH_3 from its elements in this temperature range.

Sol. We know $\log_{10} \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\log \frac{0.144}{1.64} = \frac{\Delta H}{2.303 \times 1.987 \times 10^{-3}} \left(\frac{1}{673} - \frac{1}{773} \right)$$

$$\Delta H = -25.14 \text{ kcal for 2 mol} = -12.57 \text{ kcal mol}^{-1}$$

ILLUSTRATION 7.118

For the reaction $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$, the equilibrium constant is 2.8×10^{-5} at 300 K and 7.0×10^{-1} at 400 K. What is the activation energy for the reaction?

Sol. Given $K_1 = 2.8 \times 10^{-5}$ at $T_1 = 300$ K

$K_2 = 7.0 \times 10^{-1}$ at $T_2 = 400$ K

Using expression

$$\ln(K) = \frac{-E_a}{RT}$$

We get,

$$\ln(2.8 \times 10^{-5}) = \frac{-E_a}{R(300K)} + \text{Constant} \quad \dots(i)$$

$$\ln(7.0 \times 10^{-1}) = \frac{-E_a}{R(400K)} + \text{Constant} \quad \dots(ii)$$

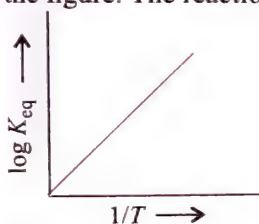
Subtracting (i) from (ii), we get

$$\begin{aligned} \ln\left(\frac{7.0 \times 10^{-1}}{2.8 \times 10^{-5}}\right) &= \frac{E_a}{R} \left(\frac{1}{300K} - \frac{1}{400K} \right) \\ &= \frac{E_a}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{100}{300 \times 400} \right) \end{aligned}$$

$$\begin{aligned} \therefore E_a &= (8.314) \left(\frac{300 \times 400}{100} \right) \left[2.303 \log \left(\frac{7.0 \times 10^{-1}}{2.8 \times 10^{-5}} \right) \right] \\ &= 101048 \text{ J mol}^{-1} = 101.048 \text{ K J mol}^{-1} \end{aligned}$$

ILLUSTRATION 7.119

A schematic plot of $\log K_{eq}$ vs inverse of temperature for a reaction is shown in the figure. The reaction must be:



- Exothermic
- Endothermic
- One with negligible enthalpy change
- Highly spontaneous at ordinary temperature

Sol. a. $K_c = Ae^{-\Delta H^\circ/RT}$

$$\log_{10} K_{eq} = \log_{10} A - \frac{\Delta H^\circ}{2.303RT}$$

$$Y = C + MX$$

Slope of the line will be positive, when $\Delta H^\circ = -ve$, i.e., the reaction is exothermic.

ILLUSTRATION 7.120

For the reaction



K is 0.63 at 27°C and 1.26 at 927°C .

- What is the average ΔH for the temperature range considered? [Use $\log 2 = 0.3$]
- What is the value of K at 1227°C ?

Sol.

- $T_1 = 1000$ K, $T_2 = 1200$ K,

$$K_1 = 0.63, K_2 = 1.26$$

Using the van't Hoff equation:

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \log_{10} \left(\frac{1.26}{0.63} \right) = \frac{\Delta H}{2.303(2)} \left(\frac{1200 - 1000}{1200 \times 1000} \right)$$

$$\Rightarrow \Delta H = 8.32 \text{ kcal mol}^{-1}.$$

- Let K_2 be the equilibrium constant at $T_2 = 1500$ K

$T_1 = 1000$ K and then $K_1 = 0.63$

$$\Rightarrow \log_{10} \left(\frac{K_2}{0.63} \right) = \frac{8.32 \times 10^3}{2.303(2)} \left(\frac{1500 - 1000}{1500 \times 1000} \right)$$

$$\Rightarrow \log_{10} \frac{K_2}{0.63} = 0.6 = \log_{10} 4$$

$$\Rightarrow K_2 = 0.63 \times 4 = 2.52$$

ILLUSTRATION 7.121

The equilibrium constant K_p for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 1.6×10^{-4} at 400°C .

What will be the equilibrium constant at 500°C if the heat of reaction in this temperature range is -25.14 kcal?

Sol. Using the relation,

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given

$$K_{p_1} = 1.6 \times 10^{-4}, \Delta H = -25.14 \text{ kcal};$$

$$R = 2 \times 10^{-3} \text{ kcal deg}^{-1} \text{ mol}^{-1}$$

$$T_1 = 400 + 273 = 673 \text{ K}; T_2 = 500 + 273 = 773 \text{ K}$$

$$\log \frac{K_{p_2}}{(1.6 \times 10^{-4})} = \frac{-25.14}{2.303 \times 2 \times 10^{-3}} \left[\frac{773 - 673}{773 \times 673} \right]$$

$$\log K_{p_2} = \log (1.6 \times 10^{-4}) - \frac{25.14 \times 10^3 \times 100}{2.303 \times 2 \times 773 \times 673}$$

$$= -3.7960 - 1.049 = -4.8450$$

$$K_{p_2} = 1.429 \times 10^{-5} \text{ atm}^{-2}$$

ILLUSTRATION 7.122

The equilibrium constant for the reaction



is 18.5 at 925 K and 9.25 at 1000 K, respectively. Calculate the enthalpy of the reaction.

Sol. Given $K_1 = 18.5$ at $T_1 = 925$

$$K_2 = 9.25 \text{ at } T_2 = 1000$$

Using the relation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000}$$

$$\text{or } \Delta H = -71080.57 \text{ J mol}^{-1}$$

7.7 APPLICATIONS OF EQUILIBRIUM CONSTANT

The equilibrium constant helps us in:

- Predicting the extent of a reaction
- Predicting the direction of the reaction
- Calculating the equilibrium concentrations

7.7.1 PREDICTING THE EXTENT OF REACTION

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples:
 - The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant, $K_c = 2.4 \times 10^{47}$.
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ at 300K has $K_c = 4.0 \times 10^{31}$.
 - $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$ at 300 K; $K_c = 5.4 \times 10^{18}$
- If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely. Consider the following examples:
 - The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$.
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$, at 298 K has $K_c = 4.8 \times 10^{-31}$.
- If K_c is in the range of 10^{-3} to 10^3 , appreciable concentrations of both reactants and products are present. Consider the following examples:
 - For reaction of H_2 with I_2 to give HI , $K_c = 57.0$ at 700 K.
 - Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2 .

These generalisations are illustrated in Fig. 7.7

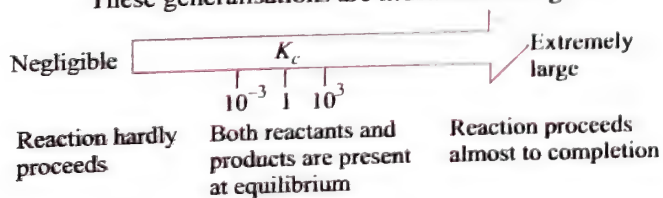


Fig. 7.7 Dependence of extent of reaction on K_c .

The value of K also gives us an idea about the relative stabilities of reactants and products. If the value of K is large, the products are more stable whereas if K is small the reactants are more stable.

7.7.2 PREDICTING THE DIRECTION OF THE REACTION

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the reaction quotient Q . The reaction quotient, Q (Q_c with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values. For a general reaction



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

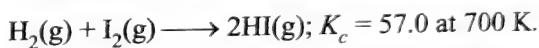
Then,

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).

If $Q_c = K_c$, the reaction mixture is already at equilibrium.

For example, consider the gaseous reaction of H_2 with I_2 .



Suppose we have molar concentrations $[\text{H}_2]_t = 0.10 \text{ M}$, $[\text{I}_2]_t = 0.20 \text{ M}$, and $[\text{HI}]_t = 0.40 \text{ M}$. (The subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t , not necessarily at equilibrium.)

Thus, the reaction quotient Q_c at this stage of the reaction is given by,

$$Q_c = \frac{[\text{HI}]_t^2}{[\text{H}_2]_t [\text{I}_2]_t} = \frac{(0.40)^2}{(0.10) \times (0.20)} = 8.0$$

Now, in this case, Q_c (8.0) does not equal K_c (57.0), so the mixture of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ is not at equilibrium; that is, more $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ will react to form more $\text{HI}(\text{g})$ and their concentrations will decrease till $Q_c = K_c$.

The reaction quotient Q_c is useful in predicting the direction of reaction by comparing the values of Q_c and K_c .

Thus, we can make the following generalisations concerning the direction of the reaction (Fig. 7.8).

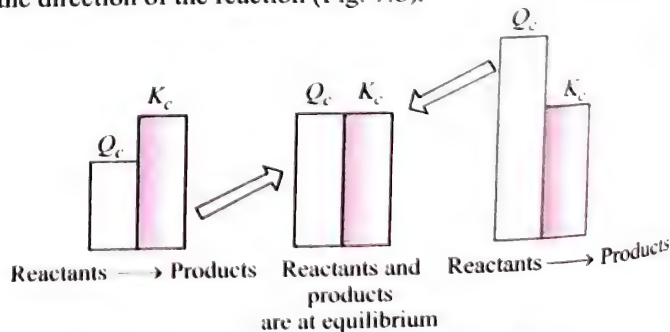


Fig. 7.8 Predicting the direction of the reaction

- If $Q_c < K_c$, net reaction goes from left to right
- If $Q_c > K_c$, the net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs.

7.7.3 CALCULATION OF EQUILIBRIUM CONCENTRATION AND EQUILIBRIUM PRESSURE

If the equilibrium concentration of various reactants and products is known in a reaction, the equilibrium constant can be calculated. On the other hand, if the equilibrium constant is known, then the equilibrium concentration can be calculated.

ILLUSTRATION 7.123

Consider the reaction



at 375°C, the value of equilibrium constant for the reaction is 0.0032. It was observed that the concentration of the three species is 0.050 mol L⁻¹ each at a certain instant. Discuss what will happen in the reaction vessel?

Sol. In this equation, concentration of three species, i.e., SO₂Cl₂(g), SO₂(g), and Cl₂(g) each is given, but it is not mentioned that whether the system is at equilibrium or not. So first check it.

Find reaction coefficient for given equation.

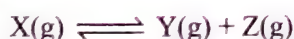
$$Q = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(0.05)(0.05)}{(0.05)} = 0.05$$

⇒ $Q \neq K_{\text{eq}}$, so system is not at equilibrium state.

As $Q > K_{\text{eq}}$, the concentration must adjust till $Q = K_{\text{eq}}$ for equilibrium. This can happen only if reaction shifts backwards, and products recombine to give back reactants. Hence, in the reaction vessel, the system will move backward so that it can achieve equilibrium state.

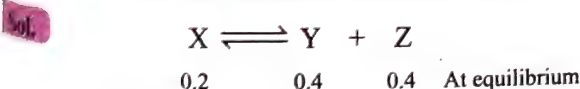
ILLUSTRATION 7.124

Consider the reaction



when the system is at equilibrium at 100°, the concentrations are found to be [X] = 0.2 M, [Y] = [Z] = 0.4 M

- If the pressure of the container is suddenly halved at 100° C, find the equilibrium concentration.
- If the pressure of the container is suddenly doubled at 100°C, find the equilibrium concentration.



$$K_c = \frac{0.4 \times 0.4}{0.2} = 0.8$$

- When pressure is halved, (i.e. $P \longrightarrow \frac{P}{2}$), concentration is halved.

$$\therefore [\text{X}] = 0.1 \text{ M}; [\text{Y}] = [\text{Z}] = 0.2 \text{ M}$$

$$Q_c = \frac{0.2 \times 0.2}{0.1} = 0.4$$

∴ $Q_c < K_c$ (Reaction goes forward)

$$K_c = 0.8 = \frac{(0.2 + x)(0.2 + x)}{(0.1 - x)}$$

Solving for x:

$$x^2 + 0.4x - 0.04 = 0$$

$$x = \frac{-0.4 + \sqrt{0.16 + 4 \times 0.04}}{2} = 0.08$$

∴ Equilibrium concentration:

$$[\text{X}] = 0.1 - x = 0.1 - 0.08 = 0.02 \text{ M}$$

$$[\text{Y}] = [\text{Z}] = 0.2 + x = 0.2 + 0.08 = 0.28 \text{ M}$$

- When pressure is doubled (i.e., $P \longrightarrow 2P$), concentration is doubled.

$$\therefore [\text{X}] = 0.4 \text{ M} \quad [\text{Y}] = [\text{Z}] = 0.8 \text{ M}$$

$$Q_c = \frac{0.8 \times 0.8}{0.4} = 1.6$$

∴ $Q_c > K_c$ (Reaction goes backward)

$$K_c = 0.8 = \frac{(0.8 - x)(0.8 - x)}{(0.4 + x)}$$

Solving for x:

$$x^2 - 0.4x + 0.32 = 0$$

$$x = \frac{-(-0.4) + \sqrt{0.16 - 1.28}}{2} \approx 0.73$$

∴ Equilibrium concentration:

$$[\text{X}] = 0.4 + x = 0.4 + 0.73 = 1.13 \text{ M}$$

$$[\text{Y}] = [\text{Z}] = 0.8 - x = 0.8 - 0.73 = 0.07 \text{ M}$$

ILLUSTRATION 7.125

The value of K_c for the reaction $2\text{A} \rightleftharpoons \text{B} + \text{C}$ is 2.0×10^{-3} . At a given time, the composition of reaction mixture is $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4} \text{ M}$. In which direction the reaction will proceed?

Sol. For the reaction $2\text{A} \rightleftharpoons \text{B} + \text{C}$,

$$K_c = 2.0 \times 10^{-3} \text{ (given)}$$

$$\text{The reaction quotient } Q_c = \frac{[\text{B}][\text{C}]}{[\text{A}]^2}$$

Substituting the value of A, B, and C, we get

$$Q_c = \frac{(3 \times 10^{-4})(3 \times 10^{-4})}{(3 \times 10^{-4})^2} = 1$$

Since $Q_c > K_c$, therefore, the reaction will proceed in the backward direction.

ILLUSTRATION 7.126

13.8 g of N₂O₄ was placed in a 1 L reaction vessel at 400 K and allowed to attain equilibrium.



The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c , K_p and partial pressure at equilibrium.

Sol. $pV = nRT$

Total volume = 1 L

Mw of N₂O₄ = 92 g

$$\text{Number of moles of the gas } (n) = \frac{13.8 \text{ g}}{92 \text{ g}} = 0.15$$

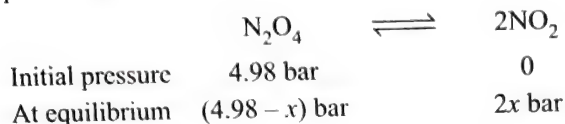
$$\text{Gas constant } (R) = 0.083 \text{ bar L mol}^{-1} \text{ K}^{-1}$$

$$\text{Temperature } (T) = 400 \text{ K}$$

$$pV = nRT$$

$$p \times 1 \text{ L} = 0.15 \text{ mol} \times 0.083 \text{ bar L mol}^{-1} \text{ K}^{-1} \times 400 \text{ K}$$

$$p = 4.98 \text{ bar}$$



Hence,

$$p_{\text{total at equilibrium}} = p_{\text{N}_2\text{O}_4} + p_{\text{NO}_2}$$

$$9.15 = (4.98 - x) + 2x$$

$$9.15 = 4.98 + x$$

$$\therefore x = 9.15 - 4.98 = 4.17 \text{ bar}$$

Partial pressures at equilibrium are,

$$p_{\text{N}_2\text{O}_4} = 4.98 - 4.17 = \mathbf{0.81 \text{ bar}}$$

$$p_{\text{NO}_2} = 2x = 2 \times 4.17 = \mathbf{8.34 \text{ bar}}$$

$$k_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{(8.34)^2}{0.81} = 85.87$$

$$k_p = k_c(RT)^{\Delta n}$$

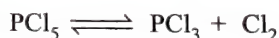
$$85.87 = k_c(0.083 \times 400)^1$$

$$\therefore k_c = 2.586 = 2.6$$

ILLUSTRATION 7.127

3.00 mole of PCl_5 kept in 1 L closed reaction vessel was allowed to attain equilibrium at 380 K. Calculate composition of the mixture at equilibrium. $K_c = 1.80$.

Sol.



$$\begin{array}{ccc} \text{Initial concentration} & 3.0 & 0 & 0 \\ \text{Concentration at equilibrium} & (3.0 - x) & x & x \end{array}$$

[Let x M of PCl_5 be dissociated]

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$1.8 = \frac{x \times x}{(3 - x)}$$

$$x^2 = 1.8x - 5.4 = 0$$

$$x = \frac{-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}}{2}$$

$$x = \frac{-1.8 \pm \sqrt{(3.24 + 21.6)}}{2}$$

$$x = \frac{-1.8 \pm 4.98}{2}$$

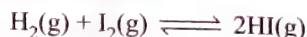
$$x = \frac{-1.8 + 4.98}{2} = 1.59$$

$$\therefore [\text{PCl}_5] = 3.0 - x = 3 - 1.59 = 1.41 \text{ M}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = x = 1.59 \text{ M}$$

ILLUSTRATION 7.128

The value of K_c for the reaction



is 64 at 773 K. If one mole of H_2 , one mole of I_2 , and three moles of HI are taken in a 1 L flask, find the concentrations of I_2 and HI at equilibrium at 773 K.

Sol. For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{3^2}{1 \times 1} = 9 [V = 1\text{L}]$$

Note: When $\Delta n_g = 0$, not only $K_p = K_c$, but volume terms always get cancelled in the expression of K .

$\Rightarrow Q < K_{\text{eq}} (=64)$. Hence, the reaction proceeds to forward direction to achieve equilibrium.

Let x mol of H_2 and I_2 combine to produce $2x$ mol of HI .

Moles	H_2	I_2	HI
Initial	1	1	3
At equilibrium	$1 - x$	$1 - x$	$3 + 2x$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 64$$

Concentration of species at equilibrium are:

$$[\text{H}_2] = (1 - x)/1, [\text{I}_2] = (1 - x)/1, [\text{HI}] = (3 + 2x)/1$$

$$K_c = \frac{\left(\frac{3 + 2x}{1}\right)^2}{\left(\frac{1 - x}{1}\right)\left(\frac{1 - x}{1}\right)} = \frac{(3 + 2x)^2}{(1 - x)^2} = 64$$

$$\Rightarrow x = 0.5$$

$$[\text{I}_2] = \frac{1 - x}{1} = 1 - 0.5 = 0.5 \text{ M}$$

$$[\text{HI}] = \frac{3 + 2x}{1} = 3 + 1.0 = 4.0 \text{ M}$$

ILLUSTRATION 7.129

In a 1.0 L aqueous solution when the reaction



reaches equilibrium, $[\text{Cu}^{2+}] = x$ M and $[\text{Ag}^+] = y$ M.

If the volume of solution is doubled by adding water, then at equilibrium:

a. $[\text{Cu}^{2+}] = \frac{x}{2} \text{ M}, [\text{Ag}^+] = \frac{y}{2} \text{ M}$

b. $[\text{Cu}^{2+}] > \frac{x}{2} \text{ M}, [\text{Ag}^+] > \frac{y}{2} \text{ M}$

c. $[\text{Cu}^{2+}] < \frac{x}{2} \text{ M}, [\text{Ag}^+] > \frac{y}{2} \text{ M}$

d. $[\text{Cu}^{2+}] < \frac{x}{2} \text{ M}, [\text{Ag}^+] < \frac{y}{2} \text{ M}$

Sol. Consider the equation



At equilibrium: $[\text{Cu}^{2+}] = x \text{ M}; [\text{Ag}^+] = y \text{ M}$

$$K_{eq} = K_c = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{x}{y^2}$$

Now volume is doubled by adding water. As a result, the concentration of ions will become half and the system will no longer be in equilibrium. In order to check the direction of equilibrium, let us find the value of reaction coefficients, Q .

$$Q = Q_c = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{x/2}{(y/2)^2} = \frac{2x}{y^2}$$

$$\Rightarrow Q > K_{eq}$$

This means that the system will move in backward direction in order to re-establish the equilibrium state.

$$\Rightarrow [Ag^+]_{At\ new\ eq} > \frac{y}{2} \text{ and } [Cu^{2+}]_{At\ new\ eq} < \frac{x}{2}$$

ILLUSTRATION 7.130

H_2 and I_2 are mixed at $400^\circ C$ in a 1.0 L container, and when equilibrium is established, the following concentrations are present: $[HI] = 0.8\text{ M}$, $[H_2] = 0.08\text{ M}$, and $[I_2] = 0.08\text{ M}$. If now an additional 0.4 mol of HI is added, what are the new equilibrium concentrations, when the new equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is reestablished?

Sol. First determine the equilibrium constant.

$$K_c \text{ for } H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.8)^2}{0.08 \times 0.08} = 100$$

When 0.4 mol of HI are added, equilibrium is disturbed

At that instant, $[HI] = 0.8 + 0.4 = 1.2\text{ M}$

$$\Rightarrow Q > K_c \text{ since } Q = \frac{(1.2)^2}{0.08 \times 0.08} = 225$$

\Rightarrow Backward reaction dominates and the equilibrium shifts to the left.

Let $2x =$ concentration of HI consumed (while going left)
Then concentration of each of H_2 and I_2 formed $= x$

$$\Rightarrow [HI] = 1.2 - 2x, [H_2] = 0.08 + x,$$

$$[I_2] = 0.08 + x \text{ and } K_c = 100$$

$$\Rightarrow K_c = \frac{(1.2 - 2x)^2}{(0.08 + x)(0.08 + x)} = 100$$

\Rightarrow Take square root on the side to get

$$x = 0.033$$

Finally, the equilibrium concentrations are:

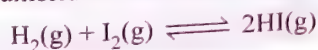
$$[HI] = 1.2 - 2x = 1.2 - 0.033 \times 2 = 1.13\text{ M}$$

$$[H_2] = 0.08 + x = 0.08 + 0.033 = 0.11\text{ M}$$

$$[I_2] = 0.08 + x = 0.08 + 0.033 = 0.11\text{ M}$$

ILLUSTRATION 7.131

At $448^\circ C$, the equilibrium constant (K_c) for the reaction



is 50.5. Predict the direction in which the reaction will proceed to reach equilibrium at $448^\circ C$, if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2 , and 3.0×10^{-2} mol of I_2 in a 2.0 L container.

Sol. The initial concentrations are

$$[HI] = \frac{2.0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 1.0 \times 10^{-2} \text{ mol L}^{-1}$$

$$[H_2] = \frac{1.0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 0.5 \times 10^{-2} \text{ mol L}^{-1}$$

$$[I_2] = \frac{3.0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 1.5 \times 10^{-2} \text{ mol L}^{-1}$$

Concentration quotient.

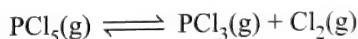
$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1.0 \times 10^{-2} \text{ mol L}^{-1})^2}{(0.5 \times 10^{-2} \text{ mol L}^{-1}) \times (1.5 \times 10^{-2} \text{ mol L}^{-1})} = 1.3$$

Since $Q < K$, the reaction will proceed in the forward direction to attain equilibrium so that Q becomes equal to K .

7.7.4 CALCULATION OF DEGREE OF DISSOCIATION USING PRESSURE-TEMPERATURE DETERMINATION

Let us consider the following reaction:



Initial pressure and temperature are P_1 and T_1 . At equilibrium, pressure and temperature are P_2 and T_2 , respectively. The volume of vessel is constant, equal to V .

	$PCl_5(g)$	\rightleftharpoons	$PCl_3(g)$	$+$	$Cl_2(g)$	n	V	T	P
$t = 0$	a		0		0	a	V	T_1	P_1
t_{eq}	$a - \alpha\alpha$		$\alpha\alpha$		$\alpha\alpha$	$a + \alpha\alpha$	V	T_2	P_2

$$\text{Initial state } P_1 V = aRT_1 \quad \dots(i)$$

$$\text{Equilibrium state } P_2 V = (a + \alpha\alpha)RT_2 \quad \dots(ii)$$

Dividing equations (i) and (ii), we get

$$\frac{P_1}{P_2} = \frac{T_1}{(1 + \alpha)T_2}$$

$$(1 + \alpha) = \frac{T_1 P_2}{T_2 P_1}$$

$$\therefore \alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

Alternatively:

$$\frac{\text{Initial moles}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure after change of temperature}}{\text{Equilibrium pressure}}$$

ILLUSTRATION 7.132

One mole of $\text{N}_2\text{O}_4(\text{g})$ at 200 K is kept in a closed container at 1.0 atm pressure. It is heated to 400 K, where 20% by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. Calculate the resultant pressure.

Sol. First method:

$$\text{Using the formula, } \alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

$$\frac{20}{100} = \frac{200 \times P_2 - 400 \times 1}{400 \times 1} \Rightarrow P_2 = 2.4 \text{ atm}$$

Alternate method:

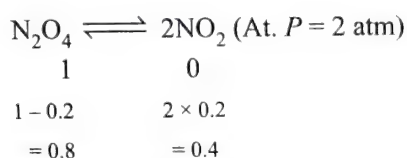
V is constant (closed container)

On doubling the temperature \Rightarrow Pressure doubles

$$\left(\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right) \Rightarrow P_2 = 2 \text{ atm}$$

Decomposition of N_2O_4 20% by mass \propto 20% by mole
(mass \propto mole)

$$\therefore \alpha = 0.2$$



$$\text{Total mole} = 0.8 + 0.4 = 1.2$$

Using the formula,

$$\frac{\text{Initial mole}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure after change of temperature}}{\text{Equilibrium pressure}}$$

$$\Rightarrow \frac{1}{1.2} = \frac{2}{P}$$

$$\Rightarrow \therefore P = 2.4 \text{ atm}$$

7.8 RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT K , REACTION QUOTIENT Q , AND GIBBS ENERGY G

The equilibrium constant K_c for a reaction does not tell anything about the rate of the reaction. Thus, K_c is independent on the rate of the reaction. However, as already studied in Chapter 6, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy ΔG , if

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then the reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG , the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, the reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G^\ominus + RT \ln Q \quad \dots(i)$$

where, G^\ominus is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the equation (i) becomes

$$\Delta G = \Delta G^\ominus + RT \ln K = 0$$

$$\Delta G^\ominus = -RT \ln K \quad \dots(ii)$$

$$\ln K = -\Delta G^\ominus / RT$$

Taking antilog of both sides, we get

$$K = e^{-\Delta G^\ominus / RT} \quad \dots(iii)$$

Hence, using equation (iii), the reaction spontaneity can be interpreted in terms of the value of ΔG^\ominus .

- If $\Delta G^\ominus < 0$, then $-\Delta G^\ominus / RT$ is positive, and $e^{-\Delta G^\ominus / RT} > 1$, making $K > 1$, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
- If $\Delta G^\ominus > 0$, then $-\Delta G^\ominus / RT$ is negative, and $e^{-\Delta G^\ominus / RT} < 1$, that is, $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

The relation between ΔG^\ominus and K as obtained from equation (ii) is given in Table 7.4.

Table 7.4 Relation between ΔG^\ominus and K

ΔG^\ominus	$\ln K$	K	Reaction
Negative	Positive	> 1	Spontaneous
Positive	Negative	< 1	Non-spontaneous
0	0	$= 1$	Equilibrium

ILLUSTRATION 7.133

The value of ΔG^\ominus for the phosphorylation of glucose in glycolysis is 13.8 kJ mol⁻¹. Find the value of K_c at 298 K.

Sol. $\Delta G^\ominus = 13.8 \text{ kJ mol} = 13.8 \times 10^3 \text{ J mol}$

Also, $\Delta G^\ominus = -RT \ln K_c$

Hence, $\ln K_c = -13.8 \times 10^3 \text{ J mol}^{-1} \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K})$

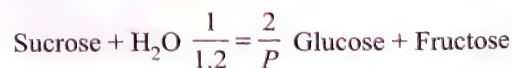
$$\ln K_c = -5.569$$

$$K_c = e^{-5.569}$$

$$K_c = 3.81 \times 10^{-3}$$

ILLUSTRATION 7.134

Hydrolysis of sucrose gives



Equilibrium constant K_c for the reaction is 2×10^{13} at 300 K. Calculate ΔG^\ominus at 300 K.

Sol. $\Delta G^\ominus = -RT \ln K_c$

$$\Delta G^\ominus = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$$

$$\Delta G^\ominus = -7.64 \times 10^4 \text{ J mol}^{-1}$$

ILLUSTRATION 7.135

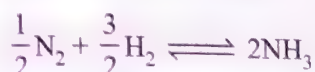
If K_c is not numerically equal to K_p , how can both of the following equations be valid?

$$\Delta G^\ominus = -2.303RT \log K_c; \Delta G^\ominus = -2.303RT \log K_p$$

Sol. ΔG^\ominus will have two different values but one refers to the standard state in which all reactants and products are 1 M and other refers to the standard state in which all reactants and products are at 1 atm.

ILLUSTRATION 7.136

The value of K_p at 298 K for the reaction

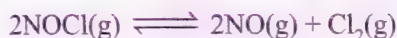


is found to be 826.0, partial pressures being measured in atmospheric units. Calculate ΔG^\ominus at 298 K.

Sol. $\Delta G^\ominus = -2.303RT \log K_p$
 $= -2.303 \times 1.98 \times 298 \times \log 826$
 $= -3980 \text{ cal.}$

ILLUSTRATION 7.137

For the reaction,



Calculate the standard equilibrium constant at 298 K. Given that the values of ΔH^\ominus and ΔS^\ominus of the reaction at 298 K are 77.2 kJ mol^{-1} and $122 \text{ J K}^{-1} \text{ mol}^{-1}$.

Sol. Using the relation

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$

$$= 77200 - 298 \times 122$$

$$= 40844 \text{ J mol}^{-1}$$

Let the equilibrium constant be K_c^\ominus . We know that

$$\Delta G^\ominus = -2.303 RT \log K_c^\ominus$$

$$\text{or } \log K_c^\ominus = -\frac{\Delta G^\ominus}{2.303 \times 8.314 \times 298}$$

$$= -\frac{40844}{2.303 \times 8.314 \times 298} = -7.158$$

$$K_c^\ominus = 6.95 \times 10^{-8}$$

ILLUSTRATION 7.138

ΔG^\ominus for $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ is $-16.5 \text{ kJ mol}^{-1}$.

Find out K_p for the reaction at 25°C . Also report K_p and ΔG^\ominus for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 25°C .

Sol. $\log K_p = -\frac{\Delta G^\ominus}{2.303RT} = -\frac{(-16.5 \times 10^3)}{2.303 \times 8.314 \times 298} = 2.8917$
 $K_p = 779.41$

K_p for reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is equal to $(779.41)^2 = 6.07 \times 10^5$

$$\Delta G^\ominus = -2.303 \times 8.314 \times 298 \log 6.07 \times 10^5 \text{ J}$$

$$= -32.998 \text{ kJ mol}^{-1}$$

ILLUSTRATION 7.139

In the following equilibrium



When 5 mol of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given: $\Delta_f G^\ominus_{\text{N}_2\text{O}_4} = 100 \text{ kJ}$, $\Delta_f G^\ominus_{\text{NO}_2} = 50 \text{ kJ}$

a. Find ΔG of the reaction at 298 K.

b. Find the direction of the reaction.

Sol. Reaction quotient $= \frac{[p_{\text{NO}_2}]^2}{[p_{\text{N}_2\text{O}_4}]} = \frac{100}{10} = 10$

$$\Delta G^\ominus_{\text{Reaction}} = 2\Delta_f G^\ominus_{\text{NO}_2} - \Delta_f G^\ominus_{\text{N}_2\text{O}_4}$$

$$= 2 \times 50 - 100 = 0$$

We know, $\Delta G = \Delta G^\ominus - 2.303RT \log_{10} Q_p$
 $= 0 - 2.303 \times 8.314 \times 298 \log 10$
 $= -5705.8 \text{ J} = -5.705 \text{ kJ}$

Negative value shows that reaction will be in forward direction.

ILLUSTRATION 7.140

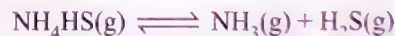
A large positive value of ΔG^\ominus corresponds to which of these?

- a. Small positive K b. Small negative K
 c. Large positive K d. Large negative K

Sol. a. Because $\Delta G^\ominus = -2.303 RT \log K$.

ILLUSTRATION 7.141

For the reaction



in a closed flask, the equilibrium pressure is $P \text{ atm}$. The standard free energy of the reaction would be:

- a. $-RT \ln p$ b. $-RT (\ln p - \ln 2)$
 c. $-2RT \ln p$ d. $-2RT (\ln p - \ln 2)$

Sol. d. $\text{NH}_4\text{HS(g)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$

$$\therefore K_p = p_{\text{NH}_3} \cdot p_{\text{H}_2\text{S}} = \frac{P}{2} \cdot \frac{P}{2} = \frac{P^2}{4}$$

$$\Delta G = -RT \ln K_p = -RT \ln \left(\frac{P^2}{4} \right)$$

$$= -RT \ln \left(\frac{P}{2} \right)^2 = -2 RT (\ln p - \ln 2)$$

ILLUSTRATION 7.142

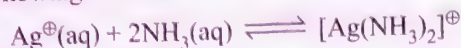
ΔG^\ominus for the reaction $X + Y \rightleftharpoons C$ is -4.606 kcal at 1000 K . The equilibrium constant for the reverse mode of the reaction will be:

- a. 100 b. 10 c. 0.01 d. 0.1

Sol. d. $-\Delta G^\ominus = 2.303RT \log K$
 $\Rightarrow 4.606 \times 10^{-3} = 2.303 \times 2 \times 1000 \log K$
 $\Rightarrow K = 10, K'(\text{reverse } r \times n) = \frac{1}{10}$

ILLUSTRATION 7.143

For the following reaction: $K = 1.7 \times 10^7$ at 25°C



What is the value of ΔG^\ominus in kJ?

Sol. a. $\Delta G^\ominus = -2.303RT \log K$
 $= -2.303 \times 8.314 \times 298.15 \log(1.7 \times 10^7)$
 $= -41.2 \text{ kJ}$

ILLUSTRATION 7.144

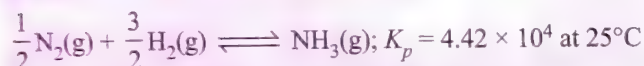
In an equilibrium reaction for which $\Delta G^\ominus = 0$, the equilibrium constant K should be equal to:

- a. Zero b. 10 c. 1 d. 2

Sol. c. $\Delta G^\ominus = -2.303RT \log K$
 when $\Delta G^\ominus = 0$ $K = 1$

ILLUSTRATION 7.145

What is ΔG^\ominus for the following reaction?



- a. $-26.5 \text{ kJ mol}^{-1}$ b. $-11.5 \text{ kJ mol}^{-1}$
 c. -2.2 kJ mol^{-1} d. $-0.97 \text{ kJ mol}^{-1}$

Sol. $\Delta G^\ominus = -2.303 RT \log K_p$
 $= -2.303 \times 8.314 \times 298.15 \times \log(4.42 \times 10^4)$
 $= -26.5 \text{ kJ mol}^{-1}$

ILLUSTRATION 7.146

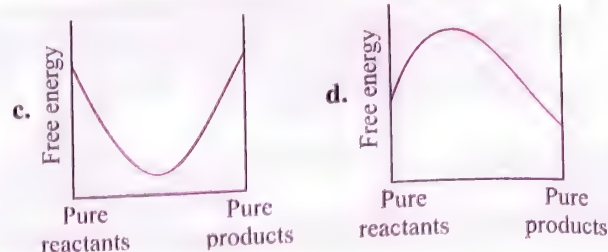
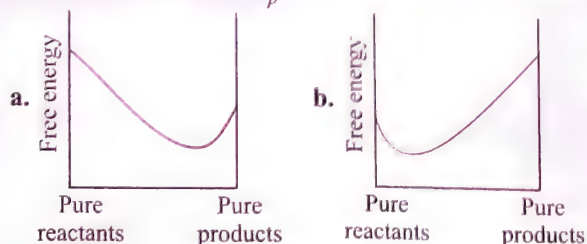
If E^\ominus_{cell} for a given reaction is negative, which gives the correct relationships for the values of ΔG^\ominus and K_{eq} ?

- a. $\Delta G^\ominus > 0, K_{\text{eq}} < 1$ b. $\Delta G^\ominus > 0, K_{\text{eq}} > 1$
 c. $\Delta G^\ominus < 0, K_{\text{eq}} > 1$ d. $\Delta G^\ominus < 0, K_{\text{eq}} < 1$

Sol. a. $\Delta G = -nFE^\ominus$ or $E^\ominus = \frac{-\Delta G}{nF}$
 $\therefore \Delta G^\ominus > 0$ and $\Delta G^\ominus = -nRT \ln K_p$
 $\therefore K_{\text{eq}} < 1$

ILLUSTRATION 7.147

Which of the following graphs correctly represent for an equilibrium reaction whose $K_p > 1$?



Sol. a.

ILLUSTRATION 7.148

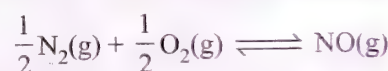
The equilibrium constant K_p for the homogeneous gaseous reaction is 10^{-3} . The standard Gibbs free energy change ΔG^\ominus for the reaction at 27°C (using $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) is

- a. Zero b. -1.8 kcal
 c. -4.154 kcal d. $+4.154 \text{ kcal}$

Sol. d. $\Delta G^\ominus = -RT \ln K_p$
 $= -2 \times 300 \times \ln(10^{-3})$
 $= +4.154 \text{ kcal}$

ILLUSTRATION 7.149

The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K ?



- a. 8.4×10^{-5} b. 7.1×10^{-9}
 c. 4.2×10^{-10} d. 1.7×10^{-19}

Sol. $\Delta G = 78 \text{ kJ mol}^{-1}$

$$T = 1000 \text{ K}$$

$$\Delta G^\ominus = -nRT \ln K_p$$

$$\therefore \ln K_p = \frac{-\Delta G^\ominus}{nRT} = \frac{-78}{8.314 \times 1000}$$

$$\text{or } K_p = \text{antilog} \left(\frac{-78}{8.314 \times 1000} \right) = 8.4 \times 10^{-5}$$

ILLUSTRATION 7.150

The densities of graphite and diamond are 22.5 and 3.51 gm cm^{-3} . The $\Delta_f G^\ominus$ values are 0 J mol^{-1} and 2900 J mol^{-1} for graphite and diamond, respectively. Calculate the equilibrium pressure for the conversion of graphite into diamond at 298 K .

Sol. We have, $C_g \longrightarrow C_d$

$$\Delta G^\ominus = \Delta G_{(\text{diamond})} - \Delta G_{(\text{graphite})}$$

$$\Rightarrow (2900 - 0) = 2900 \text{ J mol}^{-1} \therefore \Delta G^\ominus = 2900 \text{ J mol}^{-1}$$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\therefore \Delta V = (V_d - V_g) = \left(\frac{12}{3.51} - \frac{12}{2.25} \right) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$= -1.91 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

We know that,

$$(\Delta G)_T = \Delta V \partial P$$

$$\therefore \int_1^2 d(\Delta G) = \int_{P_1}^{P_2} \Delta V \partial P$$

$$\Delta G = \Delta V(P_2 - P_1)$$

$$\therefore P_2 = \frac{\Delta G}{\Delta V} + P_1$$

$$\text{or } P_2 = \frac{2900 \text{ J mol}^{-1}}{-1.91 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} + 101325 \text{ Pa}$$

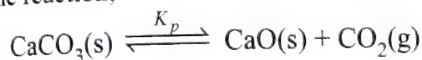
$$= 1.52 \times 10^9 \text{ Pa}$$

$$\therefore \text{Pressure} = 1.52 \times 10^9 \text{ Pa}$$

ILLUSTRATION 7.151

Calculate the pressure of CO_2 gas at 700 K in the heterogeneous equilibrium reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, if ΔG^\ominus for this reaction is $130.2 \text{ kJ mol}^{-1}$.

Sol. For the reaction,



$$K_p = P_{\text{CO}_2}$$

We know that, $\Delta G^\ominus = -RT \ln K_p$

$$\therefore \ln K_p = \frac{-\Delta G^\ominus}{RT} = -\left(\frac{130.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 700 \text{ K}} \right)$$

$$\text{or } K_p = \text{antilog} \left(\frac{-130.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 700 \text{ K}} \right)$$

$$= 1.94 \times 10^{-10} \text{ atm}$$

$$\text{or } P_{\text{CO}_2} = K_p = 1.94 \times 10^{-10} \text{ atm}$$

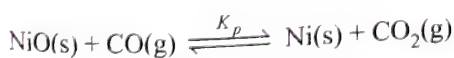
ILLUSTRATION 7.152

For the equilibrium



$\Delta G^\ominus (\text{J mol}^{-1}) = -20700 - 11.97T$. Calculate the temperature at which the product gases at equilibrium at 1 atm will contain 400 ppm of carbon monoxide.

Sol. For the given reaction,



$$\therefore K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$$

Since $P_{\text{CO}} \ll P_{\text{CO}_2}$, hence

$$K_p = \frac{1}{P_{\text{CO}}} = \frac{1}{400 \times 10^{-6}} = 2500$$

We know, $\Delta G^\ominus = -RT \ln K_p$

$$\therefore \ln K_p = \frac{-\Delta G^\ominus}{RT} = \frac{-(-20700 - 11.97T)}{RT}$$

$$\text{or } \ln K_p = \frac{20700 + 11.97T}{RT}$$

$$\Rightarrow \ln (2500) = \frac{20700 + 11.97T}{8.314 \times T}$$

$$\Rightarrow \ln (2500) (8.314T) = 20700 + 11.97T$$

$$\Rightarrow 65.049T = 20700 + 11.97T$$

$$\Rightarrow 65.049T - 11.97T = 20700$$

$$\Rightarrow 53.079T = 20700$$

$$\text{or } T = \frac{20700}{53.079} \approx 389.9 \text{ K}$$

$$\therefore \text{Temperature at equilibrium} = 389.9 \text{ K}$$

ILLUSTRATION 7.153

K_c for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ in chloroform at 291 K is 1.14. Calculate the free energy change of the reaction when the concentration of the two gases are 0.5 mol dm^{-3} each at the same temperature. ($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$).

Sol. From the given data

$$T = 291 \text{ K}; R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.14; C_{\text{NO}_2} = C_{\text{N}_2\text{O}_4} = 0.5 \text{ mol dm}^{-3}$$

The reaction quotient Q_c for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$,

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.5 \times 0.5}{0.5} = 0.5$$

Since $Q_p = Q_c(RT)^{\Delta n}$ and $\Delta n = 2 - 1 = 1$ in this case

$$\therefore Q_p = 0.5(0.082 \times 291) = 11.93$$

$$K_p = K_c(RT)^{\Delta n} = 1.14(0.082 \times 291) = 27.1$$

Substituting these values in the following equation, we get

$$\Delta G = \Delta G^\ominus + RT \ln Q_p$$

$$= -RT \ln K_p + RT \ln Q_p$$

$$= -2.303RT(\log K_p - \log Q_p)$$

$$\Delta G = -(0.082 \times 291 \times 2.303)(\log 27.2 - \log 11.93)$$

$$= -54.95(1.4346 - 1.0766) = -19.67 \text{ L atm}$$

ILLUSTRATION 7.154

A reaction mixture containing H_2 , N_2 , and NH_3 has partial pressures 2 atm, 1 atm, and 3 atm, respectively, at 725 K. If the value of K_p for the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is $4.28 \times 10^{-5} \text{ atm}^{-2}$ at 725 K, in which direction the net reaction will go?

- Forward
- Backward
- No net reaction
- Direction of reaction cannot be predicted.

Sol. $Q_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2} \times (P_{\text{H}_2})^3} = \frac{(3)^2}{(1)(2)^3} = \frac{9}{8} \text{ atm}^{-2} = 1.125 \text{ atm}^{-2}$

Since the value of Q_p is larger than K_p ($4.28 \times 10^{-5} \text{ atm}^{-2}$), it indicates net reaction will proceed in the backward direction.

Illustration Based on Degree of Dissociation using Pressure Temperature Determination

ILLUSTRATION 7.155

i. The initial pressure of PCl_5 present in one litre vessel at 200 K is 2 atm. At equilibrium the pressure increases to 3 atm with temperature increasing to 250. The percentage dissociation of PCl_5 at equilibrium is

- a. 30% b. 60% c. 0.2% d. 20%

ii. One mole of $\text{N}_2\text{O}_4(\text{g})$ at 100 K is kept in a closed container at 1.0 atm pressure. It is heated to 300 K, where 30% by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. The resultant pressure will be

- a. 3.9 atm b. 1.95 atm c. 1.0 atm d. 3.0 atm

Sol. i. d.

First method:

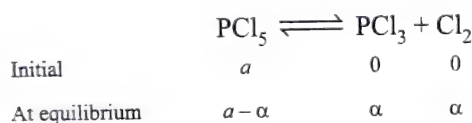
Pressure at 200 K = 2 atm

Pressure at 250 K = P atm

Using relation;

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{P}{250} = \frac{2}{200}$$

$$\therefore P = 2.5 \text{ atm}$$



$$\text{Total moles} = a + \alpha$$

$$\frac{\text{Initial mole}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure after change of temperature}}{\text{Equilibrium pressure}}$$

$$\frac{a}{a + \alpha} = \frac{2.5}{3} \Rightarrow \alpha = \frac{1}{5}a$$

$$\begin{aligned} \text{Therefore, \% of } \text{PCl}_5 \text{ dissociated} &= \frac{\alpha}{a} \times 100 \\ &= \frac{a}{5 \times a} \times 100 = 20\% \end{aligned}$$

Second method:

Using relation:

$$\begin{aligned} \alpha &= \frac{T_2 P_2 - T_1 P_1}{T_2 P_1} \\ &= \frac{200 \times 3 - 250 \times 2}{250 \times 2} = \frac{600 - 500}{500} \\ \alpha &= \frac{1}{5} \end{aligned}$$

$$\% \text{ of } \alpha = \frac{1}{5} \times 100 = 20\%$$

ii. a. **First method:**

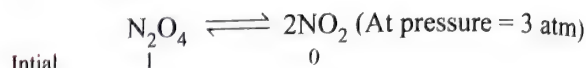
V is constant (closed container)

On tripling the temperature \Rightarrow Pressure becomes three times

$$\left(\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right) \Rightarrow P = 3 \text{ atm}$$

Decomposition of N_2O_4 30% by mass \propto 30% by mole (mass \propto mole)

$$\therefore \alpha = \frac{30}{100} = 0.3$$



$$\text{At eq} \quad 1 - 0.3 = 0.7 \quad 2 \times 0.3 = 0.6$$

$$\text{Total moles} = 0.7 + 0.6 = 1.3$$

$$\frac{\text{Initial mole}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure after change of temperature}}{\text{Equilibrium pressure}}$$

$$\frac{1}{1.3} = \frac{3}{P} \Rightarrow P = 3.9 \text{ atm}$$

Second method:

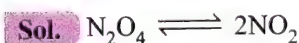
$$\alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

$$0.3 = \frac{100 \times P_2 - 300 \times 1}{300 \times 1}$$

$$\Rightarrow P_2 = 3.9 \text{ atm}$$

ILLUSTRATION 7.156

The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g L^{-1} at 288 K and 1.84 g L^{-1} at 348 K. Calculate the entropy change during the reaction at 348 K.



For K_p , proceed as follows:

$$PV = nRT = \frac{w}{m_{\text{mix}}} RT$$

$$\begin{aligned} \Rightarrow m_{\text{mix}} &= \frac{w}{V} \times \frac{RT}{P} = \frac{dRT}{P} \\ &= 3.62 \times 0.082 \times 288 = 85.6 \end{aligned}$$

Let a mol of N_2O_4 and $(1 - a)$ mol of NO_2 exist at equilibrium.

$$\therefore a \times 92 + (1 - a) \times 46 = 85.6$$

$$\therefore a = 0.86$$

$$\therefore n_{\text{N}_2\text{O}_4} = 0.86, \quad n_{\text{NO}_2} = 0.14 \text{ mol}$$

$$K_p = \frac{0.14 \times 0.14}{0.86} \times \left[\frac{1}{1} \right]^1 = 0.0228 \text{ atm at } 288 \text{ K}$$

Case II

$$m_{\text{mix}} = \frac{dRT}{P} = 1.84 \times 0.0821 \times 348 = 52.57$$

Let a mol of N_2O_4 and $(1 - a)$ mol of NO_2 exist at equilibrium.

$$\therefore a \times 92 + (1 - a) \times 46 = 52.57$$

$$\therefore a = 0.14$$

$$\therefore n_{\text{N}_2\text{O}_4} = 0.14, \quad n_{\text{NO}_2} = 0.86$$

$$\therefore K_p = \frac{0.86 \times 0.86}{0.14} \left[\frac{1}{1} \right]^1 = 5.283 \text{ atm at } 348 \text{ K}$$

$$\log_{10} \left(\frac{K_{P_2}}{K_{P_1}} \right) = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\Rightarrow \log_{10} \frac{5.283}{0.0228} = \frac{\Delta H}{2 \times 2.303} \left[\frac{348 - 288}{348 \times 288} \right]$$

$$\therefore \Delta H = 181956 \text{ cal} = 18.196 \text{ kcal}$$

$$\Delta G = -2.303 RT \log K_p$$

$$= -2.303 \times 2 \times 348 \times \log 5.283$$

$$= -1158.7 \text{ cal.}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{18195.6 + 1158.7}{348} = 55.62 \text{ cal}$$

7.9 FACTORS AFFECTING EQUILIBRIA: LE CHATELIER'S PRINCIPLE

A system in equilibrium is affected by the following factors:

- Change of concentration of any reactant or product.
- Change of pressure on the system
- Change of temperature of the system
- Addition of catalyst
- Addition of some inert gas

On changing the above factors for any reaction at equilibrium, the equilibrium of the system changes. In order to decide what course the reaction adopts and make a quantitative prediction about the effect of a change in conditions on equilibrium, we use Le Chatelier's principle. It states that a

Change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

This is applicable to all physical and chemical equilibria.

7.9.1 EFFECT OF CONCENTRATION CHANGE

Consider the general reaction at equilibrium



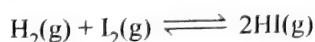
When the equilibrium is disturbed by the addition, removal of any reactant; or products. Le Chatelier's principle predicts that:

- The concentration stress of an added reactant or product is relieved by shifting net reaction in the direction that consumes the added substance.
- The concentration stress of a removed reactant or product is relieved by shifting net reaction in the direction that replenishes the removed substance.

Or in other words,

When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimise the effect of concentration changes.

Let us consider the reaction



If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed i.e., more

of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig. 7.9). This is in accordance with the Le Chatelier's principle which implies that in case of addition of a reactant or product, a new equilibrium will be set up in which the concentration of the reactant or product should be less than what it was after the addition but more than what it was in the original mixture.

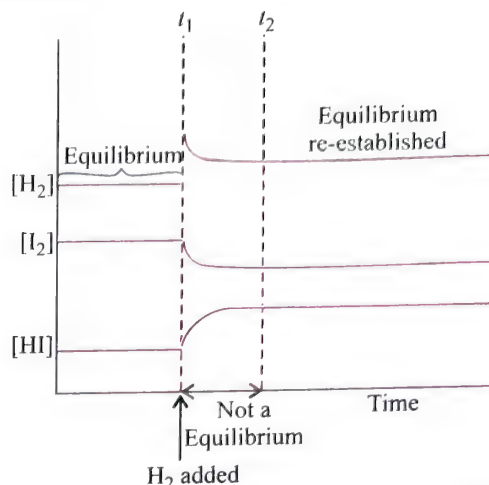
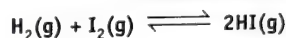


Fig. 7.9 Effect of addition of H_2 on change of concentration of the reactants and products in the reaction

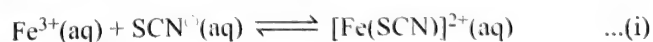


This can also be explained in terms of the reaction quotient Q_c

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

The addition of H_2 at equilibrium results in decrease in the value of Q_c and it is less than K_c . Thus, in order to attain equilibrium, the reaction proceeds in a direction where in H_2 is consumed, i.e., more of H_2 and I_2 react to form HI . Similarly, the removal of a product also increases the forward reaction and increases the concentration of products. This has a great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of the manufacture of ammonia, it is liquified and removed from the reaction mixture so that the reaction keeps moving in the forward direction. Similarly, in the large-scale production of CaO (used as important building material) from CaCO_3 , constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and the reaction continues to move in the forward direction.

The effect of concentration change on a reaction in equilibrium can be demonstrated in the laboratory with the help of the following reaction:



Yellow Colourless Deep red

$$K_c = \frac{[\text{Fe}(\text{SCN})^{2+}(\text{aq})]}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^{-}(\text{aq})]}$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocyanate solution to 1 mL of 0.2 M iron (III) nitrate solution due to the formation of $[\text{Fe}(\text{SCN})]^{2+}$. The intensity

of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^- ions. For example, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) reacts with Fe^{3+} ions to form the stable complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, thus decreasing the concentration of free $\text{Fe}^{3+}(\text{aq})$. In accordance with the Le Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[\text{Fe}(\text{SCN})]^{2+}$ to replenish the Fe^{3+} ions. Because the concentration of $[\text{Fe}(\text{SCN})]^{2+}$ decreases, the intensity of red colour decreases.

Addition of aqueous HgCl_2 also decreases red colour because Hg^{2+} reacts with SCN^- ions to form stable complex ion $[\text{Hg}(\text{SCN})_4]^{2-}$. Removal of free $\text{SCN}^-(\text{aq})$ shifts the equilibrium in equation (i) from right to left to replenish SCN^- ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

7.9.2 EFFECT OF PRESSURE CHANGE

The change in pressure has significant effect only on gaseous equilibrium which proceeds with a change in the number of moles of the gases.

The change in pressure obtained by changing the volume can effect the yield of products where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. According to Le Chatelier's principle, increase of external pressure should affect the equilibrium in such a way to reduce the pressure. This implies that the equilibrium will shift in the direction which has smaller number of moles of the gaseous substance.

Consider the reaction



Here, 4 mol of gaseous reactants ($\text{CO} + 3\text{H}_2$) becomes 2 mol of gaseous products ($\text{CH}_4 + \text{H}_2\text{O}$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one-half of its original volume. Then, the total pressure will be doubled (according to $PV = \text{constant}$). The partial pressure and therefore concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since the pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Q_c . Let $[\text{CO}]$, $[\text{H}_2]$, $[\text{CH}_4]$, and $[\text{H}_2\text{O}]$ be the molar concentrations at equilibrium for methanation reaction. When, volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

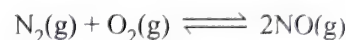
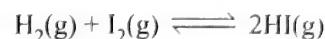
$$Q_c = \frac{[\text{CH}_4(\text{g})][\text{H}_2\text{O}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^3}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

In reaction $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

On the other hand, decrease in pressure shifts the equilibrium in favour of forward reaction.

Now, let us consider some reactions which do not involve any change in the number of moles of gaseous species:



In such reactions, pressure does not have any effect on equilibrium.

Let us consider the equilibrium involving dissolution of CO_2 in water. The equilibrium may be represented as:



On increasing the pressure of CO_2 , the equilibrium shifts in the direction which results in the decrease in pressure of CO_2 . The pressure of CO_2 will be lowered only if $\text{CO}_2(\text{g})$ dissolves in water to form $\text{CO}_2(\text{aq})$. Thus, the solubility of gas in liquid solvent is directly proportional to the pressure of the gas.

The effect of pressure is listed in Table 7.5.

Table 7.5 Effect of pressure (or volume)

Type of reaction	Effect of pressure (or volume)
Type I: $\Delta n = 0$	Equilibrium is not affected
Type II: $\Delta n = +ve$	Increase in P (or decrease in V) shifts the equilibrium to left
$\Delta n = -ve$	Increase in P (or decrease in V) shifts the equilibrium to right

In general, low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no change in the total number of moles.

7.9.3 EFFECT OF TEMPERATURE CHANGE

Whenever an equilibrium is disturbed by a change in the concentration, pressure, or volume, the composition of the equilibrium mixture changes because the reaction quotient Q_c no longer equals the equilibrium constant K_c . However, when a change in temperature occurs, the value of equilibrium constant K_c is changed.

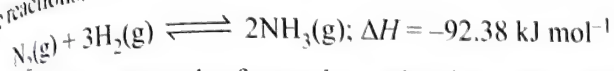
In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.

- The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

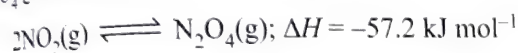
For example, production of ammonia can be represented by the reactions.



In this reaction, the forward reaction is exothermic and according to Le Chatelier's principle, increasing the temperature shifts the equilibrium in backward direction and decreases the equilibrium concentration of ammonia. On decreasing the temperature, the equilibrium shifts towards exothermic reaction. So, low temperature favours the formation of ammonia.

Effect of temperature change in exothermic reaction

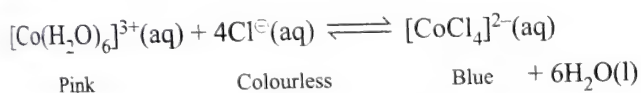
The reaction in which $\text{NO}_2(\text{g})$ (brown in colour) dimerises into N_2O_4 gas (colourless) is exothermic.



(Brown) (Colourless)

At low temperature, the forward reaction of formation of N_2O_4 is preferred, as reaction is exothermic, and thus, intensity of brown colour due to NO_2 decreases while high temperature favours the reverse reaction of formation of NO_2 , and thus, the brown colour intensifies.

Effect of temperature can also be seen in an endothermic reaction.



Pink

Colourless

Blue

At room temperature, the equilibrium mixture is blue due to $[\text{CoCl}_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$.

7.9.4 EFFECT OF A CATALYST

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

A German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory

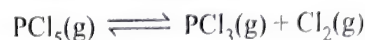
rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500°C and 200 atm.

7.9.5 EFFECT OF INERT GAS ADDITION

The effect of addition of inert gas (i.e., a gas which does not react with any of species involved in equilibrium) on equilibrium depends upon the conditions of equilibrium as discussed below:

Consider the dissociation equilibrium



The equilibrium constant, $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

a. Addition of Inert gas at constant volume: If the volume is constant ($\Delta V = 0$) and an inert gas such as argon is added, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction.

b. Addition of inert gas at constant pressure: If inert gas is added to the system at constant pressure, it will result in the increase in volume. As a consequence of this, the number of moles per unit volume of various reactants and products will decrease. According to the Le Chatelier's principle, to counterbalance this stress, the equilibrium will shift to the side where number of moles are increased. In the above given equilibrium, the addition of inert gas at constant pressure will push the equilibrium to the forward direction.

Table 7.6 illustrates the effect of addition of inert gas on equilibrium.

Table 7.6 Effect of addition of inert gas

Type of reaction	Effect of addition of inert gas
Type I: $\Delta n = 0$	Equilibrium is not affected either at constant pressure or at constant volume
Type II: $\Delta n = +ve$	At constant volume: Equilibrium is not affected At constant pressure; Equilibrium shifts to right
$\Delta n = -ve$	At constant volume; Equilibrium is not affected At constant pressure; Equilibrium shifts to left

ILLUSTRATION 7.157

- I. Which of the following conditions help melting of ice?
- High pressure, temperature below 0°C .
 - High pressure, temperature above 0°C .
 - Low pressure, temperature above 0°C .
 - Low pressure, temperature below 0°C .

- II. Densities of diamond and graphite are 3.5 and 2.3 g mL^{-1} , respectively. The increase of pressure on the equilibrium



- Favours backward reaction
 - Favours forward reaction
 - Have no effect
 - Increases the reaction rate
- III. K_p for an endothermic chemical reaction is 10 atm . Then backward reaction is favoured at

- High pressure, high temperature
- High pressure, low temperature
- Low pressure, high temperature
- Low pressure, low temperature

- IV. For the following reaction, the value of K changes with



- Change in pressure
- Change in concentration of oxygen
- Introduction of $\text{NO}(\text{g})$
- Change in temperature

- V. Which among the following reactions is favoured in forward direction by increase of temperature?

- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + 22.9 \text{ kcal}$
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) - 42.8 \text{ kcal}$
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) + 45.3 \text{ kcal}$
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) - 44 \text{ kcal} \rightleftharpoons 2\text{HCl}(\text{g})$

Sol.

- Melting of ice is favoured at high pressure and high temperature.
- Le-Chatelier's principle is not valid for solid-solid equilibrium.
- Low pressure and low temperature.
-
- It is an endothermic reaction, hence the rise in temperature will favour forward direction.

ILLUSTRATION 7.15B

- I. The exothermic formation of ClF_3 is represented by the equation:



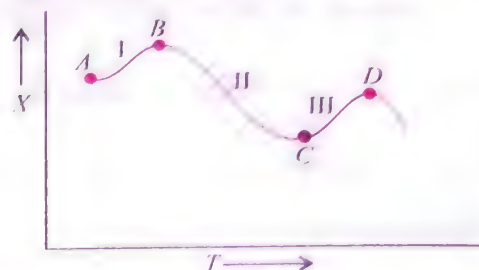
Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 , and ClF_3 ?

- Increasing the temperature
- Removing Cl_2
- Increasing the volume of the container
- Adding F_2

- II. For the following reaction through stages I, II, and III



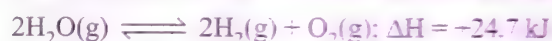
quantity of the product formed (x) varies with temperature (T) as given. Select the correct statement.



- Stages I and III are endothermic but II is exothermic.
 - Stages I and III are exothermic but II is endothermic.
 - Stages II and III are exothermic but I is endothermic.
 - Stage I is exothermic but stages II and III are endothermic.
- III. Which among the following reactions will be favoured at low pressure?

- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

- IV. Consider the following reversible reaction at equilibrium:



Which one of the following changes in conditions will lead to maximum decomposition of $\text{H}_2\text{O}(\text{g})$?

- Increasing both temperature and pressure
 - Decreasing temperature and increasing pressure
 - Increasing temperature and decreasing pressure
 - Increasing temperature at constant pressure
 - Increasing pressure at constant temperature
- V. A gas X when dissolved in water, heat is evolved. Then solubility of X will increase at
- Low pressure, high temperature
 - Low pressure, low temperature
 - High pressure, high temperature
 - High pressure, low temperature

Sol.

- Equilibrium will shift in the forward direction by increasing the concentration of reactant.
- Stage I (A to B):** The quantity of B is more than that of A. This means formation of B is favoured with increase in temperature T . Thus, stage I must be endothermic.

Stage II (B to C): The quantity of C is less than that of B. Thus, the formation of C is less favoured with an increase in temperature. Hence, stage II must be exothermic.

Stage III (C to D): Following the above statements, stage III must be endothermic.

- III. c. On lowering the pressure, equilibrium favours the direction of higher volume.
- IV. c. Reaction is endothermic and $\Delta n > 0$, hence the formation of product will be favoured by increasing the temperature and decreasing the pressure.
- V. d. $X(g) + \text{water} \rightleftharpoons X(aq) + \text{heat}$
- Exothermic reactions are favoured at low temperature (As per Le-chatelier's principle)
 - Since there is a decrease in volume in the forward direction, it will be favoured at high pressure.

ILLUSTRATION 7.159

- I. $\text{Au}(s) \rightleftharpoons \text{Au}(l)$
above mentioned equilibrium is favoured at
- High pressure, low temperature
 - High pressure, high temperature
 - Low pressure, high temperature
 - Low pressure, low temperature
- II. What is the direction of a reversible reaction when one of the products of the reaction is removed?
- The reaction moves towards right hand side.
 - The reaction moves towards left hand side.
 - The reaction moves equally on both the sides.
 - The reaction stops.
- III. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause
- Amount of solid to decrease.
 - Amount of liquid to decrease.
 - Temperature to rise.
 - Temperature to fall.
- IV. The equilibrium constant for the reaction, $A + B \rightleftharpoons C + D$ is 2.85 at room temperature and 1.4×10^{-2} at 698 K. This shows that the forward reaction is
- Exothermic
 - Endothermic
 - Unpredictable
 - There is no relationship between ΔH and K .
- V. Le Chatelier's principle is applicable to:
- Only homogeneous chemical reversible reactions
 - Only heterogeneous chemical reversible reactions
 - Only physical equilibria
 - All system, chemical or physical, in equilibrium

Sol.

- I. c. $\text{Au}(s) + \text{heat} \rightleftharpoons \text{Au}(l)$
- There is an increase in volume in the forward direction, hence the melting is favoured at low pressure.
 - Since melting is an endothermic process, it is favoured at high temperature.

- II. a. Removal of one product will result in decrease in the concentration of products and hence the reaction shifts to forward direction.
- III. a. On increasing the temperature, solid melts to liquid.
- IV. a. Because equilibrium constant decreases on increasing temperature
- V. d.

ILLUSTRATION 7.160

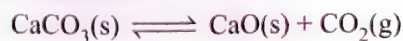
- I. Solubility of a gas in liquid increases on
- Addition of a catalyst
 - Decreasing of pressure
 - Increasing of pressure
 - Increasing of temperature
- II. When any system in equilibrium is subjected to a change in pressure, concentration, or temperature, the equilibrium is shifted in the direction which tends to undo the effect of the change. This statement is known as
- First law of thermodynamics
 - Le Chatelier's principle
 - Hess's law
 - Ostwald's law
- III. The equilibrium constant for the reaction $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ is 4.0×10^{-4} at 2000 K. In the presence of a catalyst, the equilibrium is attained 10 times faster. Therefore, the equilibrium constant in presence of the catalyst at 2000 K is
- 4×10^{-4}
 - 40×10^{-4}
 - 4×10^{-2}
 - Difficult to compute without more data
- IV. When KOH is dissolved in water, heat is evolved. If the temperature is raised, the solubility of KOH
- Increases
 - Decreases
 - Remains the same
 - Cannot be predicted
- V. Le Chatelier's principle is not applicable to
- $\text{Fe}(s) + \text{S}(s) \rightleftharpoons \text{FeS}(s)$
 - $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
 - $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
 - $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$

Sol.

- I. c.
- II. b.
- III. a. Equilibrium constant will remain same, because catalyst increases both the forward reaction as well as backward reaction.
- IV. b. Because it is an exothermic reaction.
- V. a.

ILLUSTRATION 7.161

- I. Consider the reaction



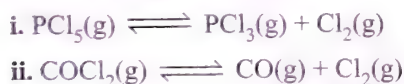
in closed container at equilibrium. What would be the effect of addition of CaCO_3 on the equilibrium concentration of CO_2 ?

- Increase
 - Decreases
 - Remains unaffected
 - Data is not sufficient to predict it
- II. The equilibrium constant for a reaction $A + B \rightleftharpoons C + D$ is 1×10^{-2} at 298 K and is 2 at 273 K. The chemical process resulting in the formation of C and D is
- Exothermic
 - Endothermic
 - Unpredictable
 - There is no relationship between ΔH and K.
- III. In a flask, colourless N_2O_4 is in equilibrium with brown-coloured NO_2 . At equilibrium, when the flask is heated to 100°C the brown colour deepens and on cooling, the brown colour became less coloured. The change in enthalpy ΔH for the system is
- Negative
 - Positive
 - Zero
 - Not defined
- IV. Consider the following equilibria:



Which of the above will be disturbed by an increase in pressure?

- II
 - I, II
 - I, II, III
 - None of these
- V. The following two reactions:



are simultaneously in equilibrium in a container at constant volume. A few moles of $\text{CO}(g)$ are later introduced into the vessel. After some time, the new equilibrium concentration of

- PCl_5 will remain unchanged
- Cl_2 will be greater
- PCl_5 will become greater
- PCl_5 will become less

Sol.

- c.
- a. The reaction is exothermic because on decreasing the temperature, the value of equilibrium constant increases.
- c. The reaction is endothermic in nature because on decreasing temperature the reaction becomes slow.
- d. Because in all the above processes, the reactants and products are in solid and liquid state which are incompressible and has no effect of pressure.
- d. $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$... (i)
 $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$... (ii)

Adding $\text{CO}(g)$ shifts reaction (ii) in the backward direction. This in turn decreases $\text{Cl}_2(g)$ which causes relation (i) to shift in forward direction and therefore concentration of PCl_5 will decrease.

ILLUSTRATION 7.162

- I. The oxidation of SO_2 by O_2 to SO_3 is an exothermic process. The yield of SO_3 is maximum if
- Temperature is increased and pressure is kept constant
 - Temperature is reduced and pressure is kept constant
 - Pressure is increased
 - Temperature and pressure both are increased

The correct option is:

- i, ii
- i, iii
- ii, iii
- ii, iii, iv

- II. The position of equilibrium will shift, by the addition of inert gas at constant pressure condition, in the following case(s):

- $\text{N}_2(g) + 3\text{F}_2(g) \rightleftharpoons 2\text{NF}_3(g)$; forward direction
- $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$; forward direction
- $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$; backward direction
- $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}(g)$; forward direction

- III. COCl_2 gas decomposes as:



If one mole of He gas is added in the vessel at equilibrium at constant pressures then

- $[\text{COCl}_2]$ increases.
- Moles of CO will increase.
- The reaction goes in forward direction.
- $K_c = 1$.

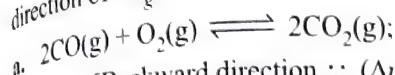
- IV. What would be the effect of increasing the volume of each of the following systems at equilibrium?

- $2\text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g)$
- $\text{Ni}(s) + 4\text{CO}(g) \rightleftharpoons \text{Ni}(\text{CO})_4(g)$
- $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

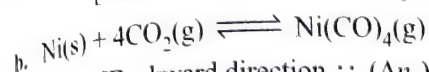
Sol.

- c. $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g)$; $\Delta H = -ve$
 and $\Delta n = n_p - n_R = 2 - 3 = -1$
 Therefore, SO_3 will be more at low T and high P .
- b., d. At constant pressure, adding inert gas result, shifting system to more in a direction where there is an increase in number of moles is $\Delta n_g > 0$.
- b., c.
 $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$; $\Delta n_g = 2 - 1 = 1$
 When an inert gas is added at constant P , the reaction shifts where $\Delta n_g > 0$ (forward direction).
 Hence, (b), (c) are correct.
- Increasing volume (at constant temperature) will result in a decrease in the concentration of all the gases. As per Le Chatelier's Principle, the reaction should move in a

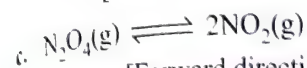
direction of increase in total number of gaseous moles (thereby increasing concentration). Thus, the shift is in a direction of $\Delta n_g > 0$.



[Backward direction $\therefore (\Delta n_g)_{\text{Backward direction}} > 0$]



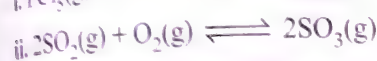
[Backward direction $\therefore (\Delta n_g)_{\text{Backward direction}} > 0$]



[Forward direction $\therefore (\Delta n_g)_{\text{Forward direction}} > 0$]

ILLUSTRATION 7.163

What happens when an inert gas is added to



at equilibrium at: (a) constant pressure and temperature, and (b) at constant volume and temperature.

Let us discuss what happens when an inert gas is added to the following reaction at equilibrium stage:



If the reaction is at equilibrium, we have:

$$K_{eq} = Q \quad \dots(i)$$

Any factor (e.g. change in the concentration of reactants/products or both) can have impact (in terms of change in the concentration of reactants/products) on that reaction at equilibrium only if that factor changes the equation (i) so that $K_{eq} \neq 0$

Two cases occur:

a. Inert gas addition at constant pressure:

$$K_{eq} = Q = \frac{P_C^p P_D^q}{P_A^m P_B^n} \quad (\text{at equilibrium})$$

and partial pressure $(p) = \chi P_{\text{Total}}$

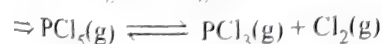
$$\left[\text{where } \chi = \frac{n}{n_{\text{Total}}} = \text{Mole fraction} \right]$$

Thus, when an inert gas is added, χ of each of the gas decreases and since P_{Total} is constant, the partial pressure decreases leading to a new equation:

$$Q < K_{eq} \text{ or } Q > K_{eq}$$

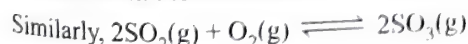
which will depend on whether

$$\Delta n_g = \sum(n_p) - \sum(n_r) < 0 \text{ or } > 0, \text{ respectively.}$$



$$\Delta n_g = 1 > 0 \Rightarrow Q < K_{eq}$$

(Reaction will move in forward direction)



$$\Delta n_g = -1 < 0 \Rightarrow Q > K_{eq}$$

(Reaction will move in the backward direction)

b. Inert gas addition at constant volume:

$$K_{eq} = Q = \frac{P_C^p P_D^q}{P_A^m P_B^n} \quad (\text{at equilibrium})$$

and partial pressure $(p) = \chi P_{\text{Total}}$

$$\left[\text{where } \chi = \frac{n}{n_{\text{Total}}} = \text{Mole fraction} \right]$$

Now, when inert gas is added at constant volume, $P_{\text{Total}} \uparrow$ and $\chi \downarrow$ but partial pressure of each gas remains same, since:

$$\text{Partial pressure } (p) = \frac{n}{n_{\text{Total}}} \cdot P_{\text{Total}} \text{ and using Dalton's}$$

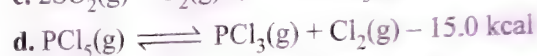
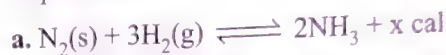
Law and ideal gas equation:

$$P_{\text{Total}} \cdot V = n_{\text{Total}} RT \quad \left[\text{Check: } \frac{P_{\text{Total}}}{n_{\text{Total}}} = \frac{RT}{V} = \text{constant} \right]$$

Thus, $K_{eq} = Q$ even on adding inert gas at constant volume. Thus, adding inert gas at constant volume has no effect on a reaction at equilibrium.

ILLUSTRATION 7.164

I. What is the effect of temperature and pressure on the yields of products?



II. What would happen to a reversible reaction at equilibrium, when

a. The temperature is raised, given that its ΔH is positive.

b. The temperature is lowered, given that its ΔH is positive.

c. The temperature is lowered, given that its ΔH is negative.

d. The pressure is lowered, given that Δn is negative.

e. The pressure is increased, given Δn is negative.

III. Which of the following factors will increase the solubility of NH_3 gas in H_2O ?

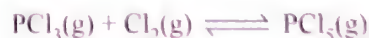
a. Increase in pressure

b. Addition of water

c. Increase in temperature

d. Decrease in pressure

IV. Consider the equilibrium



How would the following affect the position of equilibrium?

a. Addition of PCl_3

b. Addition of Cl_2

c. Removal of PCl_5

d. Decrease in the volume of container.

e. Addition of He without a change in volume

V. The reaction between H_2 and CO_2 to form CO and H_2O in the gas phase is exothermic. Predict the changes that take place when the system originally at equilibrium is stressed in each of the following ways

a. CO_2 is removed.

b. CO is removed.

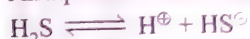
- c. The temperature is decreased.
 d. The pressure of the system is increased.
 e. The volume of the system is increased.

Sol.

- I. a. Greater yield of NH_3 at low temperature and high pressure.
 b. Greater yield of NO at high temperature. Pressure has no effect.
 c. Greater yield of SO_3 at low temperature and high pressure.
 d. Greater yield of PCl_3 and Cl_2 at high temperature and low pressure.
- II. a. More of the products will be formed.
 b. Less of the products will be formed.
 c. More of the products will be formed.
 d. Less of the products will be formed.
 e. More of the products will be formed.
- III. (a, b) $\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_3(\text{aq})$
 The solubility increases:
 • By increasing the pressure.
 • By decreasing the temperature (since dissolution of a gas is an exothermic process).
 • By adding solvent
- IV. a. Rate of forward reaction increases, more of PCl_5 is formed.
 b. Rate of forward reaction increases, more of PCl_5 is formed.
 c. More of PCl_5 is formed.
 d. More of PCl_5 is formed.
 e. No effect.
- V. a. Moves towards reactants side.
 b. Moves towards products side.
 c. Moves towards products side.
 d. Remains unchanged.
 e. Remains unchanged.

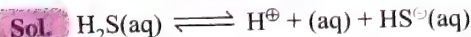
ILLUSTRATION 7.165

An aqueous solution of hydrogen sulphide shows the equilibrium:



If dilute hydrochloric acid is added to an aqueous solution of H_2S , without any change in temperature, the

- a. The equilibrium constant will change.
 b. The concentration HS^- will increase.
 c. The concentration of un-dissociated hydrogen sulphide will decrease.
 d. The concentration of HS^- will decrease.

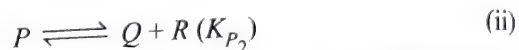


Addition of dilute $\text{HCl}(\text{aq})$ will increase the concentration of H^+ ions in the solution leading to a backward shift in the reaction to re-establish the equilibrium state. This means the concentration of $\text{HS}^-(\text{aq})$ will decrease.

7.10 RELATION BETWEEN EQUILIBRIUM CONSTANTS AND TOTAL PRESSURES OF TWO REACTIONS

The direct relation between equilibrium constants (K_{P_1} and K_{P_2}) of two reactions and total pressures of two reaction (P_1 and P_2) when degree of dissociation (α) is same for both the reactions.

Let K_{P_1} and K_{P_2} are in the ratio of x and y for the two reactions.

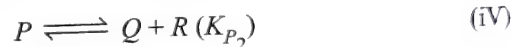


The degree of dissociation for reaction (i) and (ii) are same, then the ratio of the total pressures (P_1 and P_2) for two reaction are

$$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} = \frac{(n)^n P_1}{P_2}$$

- a. For example, for reactions, (iii) & (iv), $\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y}$.

Considering degree of dissociation is same for both the reaction.



then,
$$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} = \frac{(2)^2 P_1}{P_2}$$

If K_{P_1}/K_{P_2} for reactions (iii) and (iv) are in the ratio of 1 : 3, then P_1/P_2 is,

$$\frac{K_{P_1}}{K_{P_2}} = \frac{1}{3} = \frac{(2)^2 P_1}{P_2}$$

$$\therefore \frac{P_1}{P_2} = \frac{1}{3 \times 4} = 1 : 12$$

- b. If P_1/P_2 for reaction (iii) and (iv) are in the ratio of 2 : 3, then K_{P_1}/K_{P_2} (considering μ is same for both the reaction) is,

$$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} = \frac{(2)^2 P_1}{P_2} = \frac{4 \times 2}{3} = 8 : 3$$

$$\therefore \frac{y}{x} = \frac{K_{P_1}}{K_{P_2}} = 8 : 3$$

ILLUSTRATION 7.166

The equilibrium constants K_{P_1} and K_{P_2} for the reactions $A \rightleftharpoons 2B$ and $P \rightleftharpoons Q + R$, respectively, are in the ratio of 2 : 3. If the degree of dissociation of A and P are equal, the the ratio of the total pressure at equilibrium is,

- a. 1 : 36 b. 1 : 9 c. 1 : 6 d. 1 : 4

c. 1st method:

$$\frac{K_{p_1}}{K_{p_2}} = \frac{2}{3} = \frac{(2)^2 P_1}{P_2}; \quad P_1/P_2 = 1/6$$

IInd method:



Initial 1 0

At equilibrium $1 - \alpha$ 2α Total moles = $1 - \alpha + 2\alpha = 1 + \alpha$

$$\therefore p_A = (\text{mole fraction of } A) \times \text{Initial pressure} = \left(\frac{1 - \alpha}{1 + \alpha} \right) P_1$$

$$\text{Similarly } p_B = \left(\frac{2\alpha}{1 + \alpha} \right) P_1$$

$$\therefore K_{p_1} = \frac{(p_B)^2}{(p_A)} = \frac{\left[\left(\frac{2\alpha}{1 + \alpha} \right) P_1 \right]^2}{\left(\frac{1 - \alpha}{1 + \alpha} \right) P_1} = \frac{4\alpha^2 P_1}{(1 - \alpha^2)}$$



Initial 1 0 0

At equilibrium $1 - \alpha$ α α Total moles = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$\therefore p_P = \left(\frac{1 - \alpha}{1 + \alpha} \right) P_2; p_Q = \left(\frac{\alpha}{1 + \alpha} \right) P_2; p_R = \left(\frac{\alpha}{1 + \alpha} \right) P_2$$

$$K_{p_2} = \frac{p_R \times p_Q}{p_P} = \frac{\left(\frac{\alpha}{1 + \alpha} \right) P_2 \times \left(\frac{\alpha}{1 + \alpha} \right) P_2}{\left(\frac{1 - \alpha}{1 + \alpha} \right) P_2} = \frac{\alpha^2 P_2}{(1 - \alpha^2)}$$

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{2}{3} \text{ (given)} = \frac{4\alpha^2 P_1}{(1 - \alpha^2)} \times \left(\frac{1 - \alpha^2}{\alpha^2 P_2} \right) = \frac{4P_1}{P_2}$$

$$\therefore \frac{P_1}{P_2} = \frac{1}{6}$$

ILLUSTRATION 7.167

For the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$ occurring at two different pressure P_1 and P_2 , respectively. The ratio of the two pressure is 1 : 3. What will be the ratio of equilibrium constant, if the degree of dissociation of X and Z are equal.

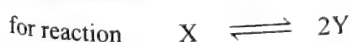
- a. 1 : 36 b. 1 : 12 c. 1 : 9 d. 4 : 3

d. 1st method:

$$\frac{K_{p_1}}{K_{p_2}} = \frac{x}{y} = \frac{(2)^2 P_1}{P_2} = 4 : 3$$

$$\therefore K_{p_1}/K_{p_2} = 4 : 3$$

IInd method:



Initial 1 0

At equilibrium $1 - \alpha$ 2α Total moles = $1 - \alpha + 2\alpha = 1 + \alpha$

$$p_X = \left(\frac{1 - \alpha}{1 + \alpha} \right) P_1; \quad p_Y = \left(\frac{2\alpha}{1 + \alpha} \right) P_1$$

$$\therefore K_{p_1} = \frac{(p_Y)^2}{p_X} = \frac{\left[\left(\frac{2\alpha}{1 + \alpha} \right) P_1 \right]^2}{\left(\frac{1 - \alpha}{1 + \alpha} \right) P_1} = \frac{4\alpha^2 P_1}{(1 - \alpha^2)} \quad \dots(i)$$



Initial 1 0 0

At equilibrium $1 - \alpha$ α α Total moles = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$p_Z = \left(\frac{1 - \alpha}{1 + \alpha} \right) P_2; p_Q = \left(\frac{\alpha}{1 + \alpha} \right) P_2; p_P = \left(\frac{\alpha}{1 + \alpha} \right) P_2$$

$$\begin{aligned} \therefore K_{p_2} &= \frac{p_P \times p_Q}{p_Z} = \frac{\left(\frac{\alpha}{1 + \alpha} \right) P_2 \times \left(\frac{\alpha}{1 + \alpha} \right) P_2}{\left(\frac{1 - \alpha}{1 + \alpha} \right) P_2} \\ &= \frac{\alpha^2 P_2}{(1 - \alpha^2)} \quad \dots(ii) \end{aligned}$$

Dividing equations (i) and (ii), we get,

$$\frac{K_{p_1}}{K_{p_2}} = \frac{4\alpha^2 P_1}{(1 - \alpha^2)} \times \left(\frac{1 - \alpha^2}{\alpha^2 P_2} \right) = \frac{4P_1}{P_2}$$

$$P_1 : P_2 = 1 : 3 \text{ (Given)}$$

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{4P_1}{P_2} = \frac{4 \times 1}{3} = 4 : 3$$

CONCEPT APPLICATION EXERCISE 7.2

Objective type

1. The yield of product in the reaction,



would be higher at:

- (1) Low temperature and high pressure
- (2) High temperature and high pressure
- (3) Low temperature and low pressure
- (4) High temperature and low pressure

2. Manufacture of ammonia from the elements is represented by



The maximum yield of ammonia will be obtained when the process is made to take place

- (1) At low pressure and high temperature
- (2) At low pressure and low temperature
- (3) At high pressure and high temperature
- (4) At high pressure and low temperature

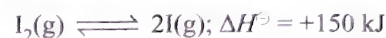
3. In the reaction,
- $2SO_2(s) + O_2(g) \rightleftharpoons 2SO_3(g) + X \text{ cal}$
- , most favourable conditions of temperature and pressure for greater yield of
- SO_3
- are

- (1) Low temperature and low pressure

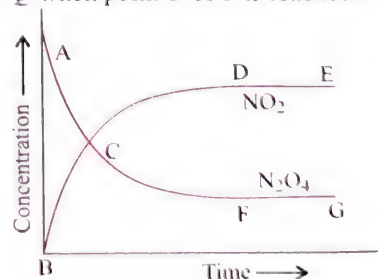
- (2) High temperature and low pressure
 (3) High temperature and high pressure
 (4) Low temperature and high pressure
4. In which of the following equilibrium, change in the volume of the system does not alter the number of moles?
- (1) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 (2) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (3) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (4) $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$
5. In the dissociation of $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$, the degree of dissociation will be affected by
- (1) Increase of temperature
 (2) Addition of an inert gas
 (3) Addition of H_2 and I_2
 (4) Increase of pressure
6. In line kilns, the following reaction,

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$
 proceeds to completion because of
- (1) High temperature
 (2) CO_2 escapes
 (3) Low temperature
 (4) Molecular mass of CaO is less than that of CaCO_3
7. Which of the following reactions will be favoured at low pressure?
- (1) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 (2) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (3) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (4) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
8. If E_f and E_r are the activation energies of forward and backward reactions and the reaction is known to be exothermic, then
- (1) $E_f > E_r$
 (2) $E_f < E_r$
 (3) $E_f = E_r$
 (4) No relation can be given between E_f and E_r
9. K_p for a reaction at 25°C is 10 atm. The activation energy for forward and reverse reactions are 12 and 20 kJ mol^{-1} respectively. The K_c for the reaction at 40°C will be:
- (1) $4.33 \times 10^{-1} \text{ M}$ (2) $3.33 \times 10^{-2} \text{ M}$
 (3) $3.33 \times 10^{-1} \text{ M}$ (4) $4.33 \times 10^{-2} \text{ M}$
10. Concentration of pure solid and liquid is not included in the expression of equilibrium constant because
- (1) Solid and liquid concentrations are independent of their quantities
 (2) Solid and liquids react slowly
 (3) Solid and liquids at equilibrium do not interact with gaseous phase
 (4) The molecules of solids and liquids cannot migrate to the gaseous phase
11. For an equilibrium reaction involving gases, the forward reaction is first order while the reverse reaction is second order. The unit of K_p for forward equilibrium is
- (1) atm (2) atm^2 (3) atm^{-1} (4) atm^{-2}

12. For the reaction, $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$, the position of equilibrium can be shifted to the right by:
- (1) Doubling the volume
 (2) Increasing the temperature
 (3) Addition of equimolar quantities of PCl_3 and PCl_5
 (4) Addition of Cl_2 at constant volume
13. The most favourable condition for the manufacture of NH_3 is:
- (1) High temperature and high pressure
 (2) Low temperature and low pressure
 (3) High temperature and low pressure
 (4) Low temperature and high pressure
14. Which of the following change will shift the reaction in forward direction?



- (1) Increase in total pressure
 (2) Increase in temperature
 (3) Increase in concentration of I
 (4) Decrease in concentration of I_2
15. In a vessel containing SO_3 , SO_2 and O_2 at equilibrium, some helium gas is introduced so that total pressure increases while temperature and volume remain the same. According to Le Chatelier's principle, the dissociation of SO_3 :
- (1) Increases (2) Decreases
 (3) Remains unaltered (4) Changes unpredictably
16. The equilibrium constants K_{p1} and K_{p2} for the reactions $\text{X} \rightleftharpoons 2\text{Y}$ and $\text{Z} \rightleftharpoons \text{P} + \text{Q}$, respectively, are in the ratio of 1:9. If the degrees of dissociation of X and Z are equal, then the ratio of total pressure at equilibria is
- (1) 1:36 (2) 1:1 (3) 1:3 (4) 1:9
17. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, $K_c = 4$. This reversible reaction is studied graphically as shown in the figure. Select the correct statements out of I, II and III.
- I: Reaction quotient has maximum value at point A
 II: Reaction proceeds left to right at a point when $[\text{N}_2\text{O}_4] = [\text{NO}_2] = 0.1 \text{ M}$
 III: $K = Q$ when point D or F is reached:



- (1) I, II (2) II, III (3) II (4) I, II, III
18. The equilibrium:

$$\text{P}_4(\text{g}) + 6\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{PCl}_3(\text{g})$$
 is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium:

- (1) $[Cl_2] > [PCl_3]$ (2) $[Cl_2] > [P_4]$
 (3) $[P_4] > [Cl_2]$ (4) $[PCl_3] > [P_4]$

ANSWERS

Objective Type

1. (1) 2. (4) 3. (4) 4. (1) 5. (1)
 6. (2) 7. (3) 8. (2) 9. (3) 10. (1)
 11. (1) 12. (4) 13. (4) 14. (2) 15. (3)
 16. (1) 17. (2) 18. (3)

Solved Examples

EXAMPLE 7.1

State which one is homogeneous or heterogeneous?

- a. $S_{\text{Rhombus}} \rightleftharpoons S_{\text{Monoclinic}}$
 b. $H_2O(l) \rightleftharpoons H_2O(v)$
 c. $H_2O(s) \rightleftharpoons H_2O(l)$
 d. $C_{\text{Diamond}} \rightleftharpoons C_{\text{Amorphous}}$
 e. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 f. $CuSO_4(s) + 3NH_3(g) \rightleftharpoons CuSO_4 \cdot 3NH_3(l)$
 g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Sol. (1) A system is said to be homogeneous if phase (P) = 1. A system with $P \geq 2$ is heterogeneous.

(2) To determine phase follow the rules given below.

System	Phase	Explanation
s + s	2	Number of solid in mixture give number of P , i.e., $P = 2$
s + l	1	Soluble systems lead to $P = 1$
s + l	2	Insoluble systems lead to $P = 2$
l + l	2	Immiscible liquids lead to $P = 2$
l + l	1	Miscible liquids lead to $P = 1$
g + g	1	All gases in a mixture give $P = 1$

Given systems a b c d e f g

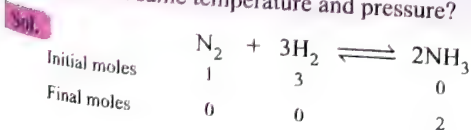
Number of phase 2 2 2 2 1 2 3

Homogeneous systems are: e,

Heterogeneous systems are: a, b, c, d, f, g

EXAMPLE 7.2

If a mixture of 3 mol of H_2 and 1 mole of N_2 is completely converted into NH_3 , what would be the ratio of the initial and final volume at same temperature and pressure?



(\therefore complete conversion)

$$\therefore \text{Ratio of initial and final volumes} = \frac{\text{Initial moles}}{\text{Final moles}}$$

$$= 4/2 = 2$$

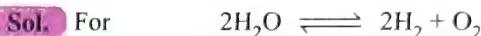
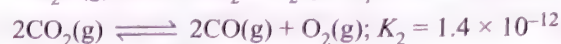
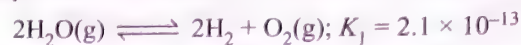
($\therefore V \propto n$, if P and T are constant)

EXAMPLE 7.3

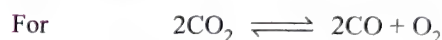
Calculate the equilibrium constant for the reaction



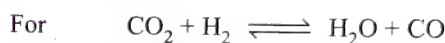
If the equilibrium constants at 1395 K for the following are:



$$K_1 = \frac{[H_2]^2 [O_2]}{[H_2O]^2} \quad \dots(i)$$



$$K_2 = \frac{[CO]^2 [O_2]}{[CO_2]^2} \quad \dots(ii)$$



$$K = \frac{[H_2O][CO]}{[CO_2][H_2]} \quad \dots(iii)$$

Thus, dividing equations (ii) by (i), we get

$$\frac{K_2}{K_1} = \frac{[CO]^2 [O_2]}{[CO_2]^2} \times \frac{[H_2O]^2}{[H_2]^2 [O_2]}$$

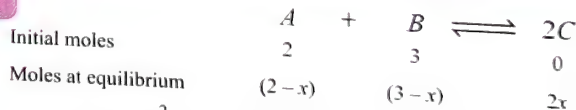
$$\frac{K_2}{K_1} = \frac{[CO]^2 [H_2O]^2}{[CO_2]^2 [H_2]^2} = K^2 \quad [\text{By equation (iii)}]$$

$$\text{or } K = \left(\frac{K_2}{K_1} \right)^{1/2} = \left(\frac{1.4 \times 10^{-12}}{2.1 \times 10^{-13}} \right)^{1/2} = 2.58$$

EXAMPLE 7.4

For the reaction, $A + B \rightleftharpoons 2C$; 2 mol of A and 3 mol of B are allowed to react. If the equilibrium constant is 4 at 400°C , what will be the moles of C at equilibrium?

Sol.



$$\therefore K_c = \frac{[C]^2}{[A][B]} = \frac{4x^2 \cdot V \cdot V}{V^2 (2-x)(3-x)} \quad [C] = \frac{2x}{V}$$

$$4 = \frac{4x^2}{(2-x)(3-x)} \quad [A] = \frac{2-x}{V}$$

$$\therefore x^2 = 6 - 5x + x^2 \quad [B] = \frac{3-x}{V}$$

$$\therefore x = 1.2$$

$$\text{Moles of } C \text{ at equilibrium} = 2x = 2 \times 1.2 = 2.4$$

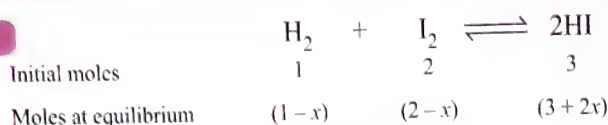
EXAMPLE 7.5

In which case does the reaction go farthest to completion: $K = 1$, $K = 10^{10}$, $K = 10^{-10}$, and why?

Sol. The ratio $\frac{[\text{Product}]}{[\text{Reactant}]}$ is maximum when $K = 10^{10}$, and thus, the reaction goes farthest to completion when $K = 10^{10}$.

EXAMPLE 7.6

One mole of H_2 , two moles of I_2 and three moles of HI are injected in one litre flask. What will be the concentration of H_2 , I_2 and HI at equilibrium at 500°C . K_c for reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 45.9.

Sol.

Let the volume of container be V L.

$$\therefore K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left[\frac{3+2x}{V}\right]^2}{\left[\frac{1-x}{V}\right]\left[\frac{2-x}{V}\right]}$$

$$45.9 = \frac{(3+2x)^2}{(1-x)(2-x)} \quad (\because K_c = 45.9)$$

$$45.9 = \frac{9+4x^2+12x}{2-3x+x^2} \quad \therefore x = 0.64$$

$$\therefore [\text{H}_2] = 1 - 0.6484 = 0.316 \text{ mol L}^{-1} (\because V = 1 \text{ L})$$

$$[\text{I}_2] = 2 - 0.684 = 1.316 \text{ mol L}^{-1}$$

$$[\text{HI}] = 3 + 2(0.684) = 4.368 \text{ mol L}^{-1}$$

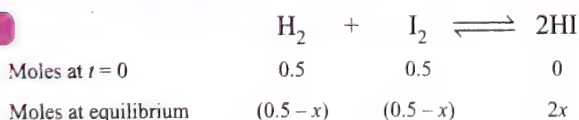
EXAMPLE 7.7

0.5 mol of H_2 and 0.5 mol of I_2 react in 10 L flask at 448°C . The equilibrium constant (K_c) is 50 for



a. What is the value of K_p ?

b. Calculate the moles of I_2 at equilibrium.

Sol.

$$\therefore K_p = K_c = \frac{4x^2}{(0.5-x)^2}$$

Note: Volume term is eliminated, if $\Delta n = 0$.

a. $K_p = K_c$ ($\because \Delta n = 0$)

$$\therefore K_p = 50$$

b. $50 = \frac{4x^2}{(0.5-x)^2}$ or $\frac{2x}{(0.5-x)} = \sqrt{50}$

$$\therefore x = 0.39$$

$$\therefore \text{Moles of } \text{I}_2 \text{ at equilibrium} = 0.50 - 0.39 = 0.11 \text{ mol}$$

EXAMPLE 7.8

The activation energy of $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ in equilibrium for the forward reaction is 167 kJ mol^{-1} whereas for the reverse reaction is 180 kJ mol^{-1} . The presence of catalyst lowers the activation energy by 80 kJ mol^{-1} . Assuming that the reactions are made at 27°C and the frequency factor for the forward and backward reactions are 6×10^{-4} and 3×10^{-3} , respectively, calculate K_c .

Sol. The lowering of activation energy by a catalyst occurs for forward reaction as well as for backward reaction.

Thus, in presence of catalyst,

$$\begin{aligned} \text{Energy of activation for forward reaction } (\Delta H_1) \\ = 167 - 80 = 37 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Energy of activation for backward reaction } (\Delta H_2) \\ = 180 - 80 = 100 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{For forward reaction, } K_1 = A_1 e^{-\Delta H_1/RT}$$

$$\text{For backward reaction } K_2 = A_2 e^{-\Delta H_2/RT}$$

where A_1 and A_2 are frequency factors and ΔH_1 and ΔH_2 are energies of activation.

$$\begin{aligned} \therefore K_c &= \frac{K_1}{K_2} = \frac{A_1}{A_2} \cdot e^{[(\Delta H_1/RT) - (\Delta H_2/RT)]} \\ &= \frac{6 \times 10^{-4}}{3 \times 10^{-3}} \times e^{[(-87+100)/(8.314 \times 10^{-3} \times 300)]} \end{aligned}$$

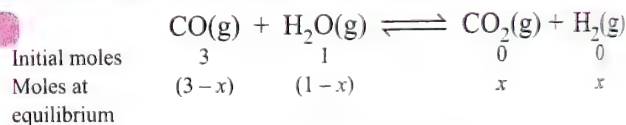
$$K_c = 2 \times 10^{-1} e^{+13/(8.314 \times 300 \times 10^{-3})} = 36.8$$

EXAMPLE 7.9

K_c for $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ at 986°C is 0.63. A mixture of 1 mol $\text{H}_2\text{O(g)}$ and 3 mol $\text{CO}_2\text{(g)}$ is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

a. How many moles of H_2 are present at equilibrium?

b. Calculate partial pressure of each gas at equilibrium.

Sol.

$$\text{Total moles at equilibrium} = 3 - x + 1 - x + x + x = 4$$

$$\text{Now, } K_c = \frac{x^2}{(3-x)(1-x)}$$

$$\therefore \frac{x^2}{3+x^2-4x} = 0.63 \quad (\because K_c = 0.63)$$

$$\therefore x = 0.681$$

$$\therefore \text{Moles of } \text{H}_2 \text{ formed} = 0.681$$

$$\text{Total pressure at equilibrium} = 2 \text{ atm;}$$

$$\text{Total moles at equilibrium} = 4$$

$$P'_g = P \times \text{Mole fraction of that gas}$$

$$\therefore P'_{\text{CO}_2} = P_{\text{H}_2} = \frac{x \cdot P}{4} = \frac{0.681 \times 2}{4} = 0.34 \text{ atm}$$

$$P'_{\text{CO}} = \frac{(3-x) \cdot P}{4} = 1.16 \text{ atm}$$

$$P'_{\text{H}_2\text{O}} = \frac{(1-x) \cdot P}{4} = 0.16 \text{ atm}$$

EXAMPLE 7.10

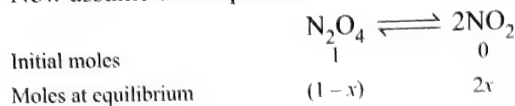
At 700 K , CO_2 and H_2 react to form CO and H_2O . For this purpose, K_c is 0.11. If a mixture of 0.45 mol of CO_2 and 0.45 mol of H_2 is heated to 700 K .

a. Find out amount of each gas at equilibrium.

b. When equilibrium has been reached, another 0.34 mol of CO_2 and 0.34 mol of H_2 are added to the reaction mixture. Find the composition of mixture at new equilibrium.

$$\therefore K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{0.3 \times 0.3}{0.7} = 0.1286 \text{ atm}$$

Now assume decomposition at 1.0 atm pressure



$$K_p = \frac{(n_{\text{NO}_2})^2}{n_{\text{N}_2\text{O}_4}} \times \left(\frac{P}{\Sigma n} \right)^{\Delta n} = \frac{(2x)^2}{(1-x)} \times \left[\frac{10}{(1+x)} \right]^1$$

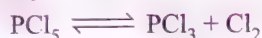
$$\text{or } 0.1286 = \frac{4x^2 \times 10}{(1-x)^2} \therefore x = 0.0565$$

$$P'_{\text{NO}_2} = \frac{2x}{(1+x)} \times P = \frac{2 \times 0.0565 \times 10}{(1+0.0565)} = 1.07 \text{ atm}$$

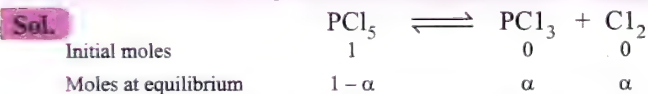
$$P'_{\text{N}_2\text{O}_2} = \left[\frac{1-0.0565}{1+0.0565} \right] \times 10 = 8.93 \text{ atm}$$

EXAMPLE 7.15

Prove $\alpha = \sqrt{\left(\frac{K_p}{P + K_p} \right)}$ for



where α is the degree of dissociation at temperature when equilibrium constant is K_p .



where α is the degree of dissociation. Total moles = $1 + \alpha$

$$\therefore P'_{\text{Cl}_2} = \left[\frac{\alpha}{1+\alpha} \right] \times P, P'_{\text{Cl}_3} = \left[\frac{\alpha}{1+\alpha} \right] \times P$$

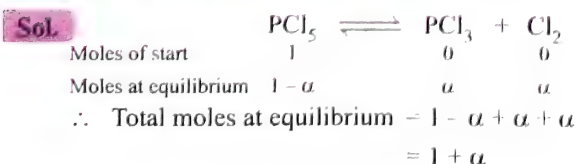
$$P'_{\text{Cl}_5} = \left[\frac{1-\alpha}{1+\alpha} \right] P$$

$$\therefore K_p = \frac{P'_{\text{Cl}_3} \times P'_{\text{Cl}_2}}{P'_{\text{Cl}_5}} = \frac{\left[\frac{\alpha \times P}{1+\alpha} \right] \left[\frac{\alpha \times P}{1+\alpha} \right]}{\left[\frac{1-\alpha}{1+\alpha} \right] P}$$

$$K_p = \frac{\alpha^2 P}{1-\alpha^2} \therefore \alpha = \sqrt{\left(\frac{K_p}{P + K_p} \right)}$$

EXAMPLE 7.16

At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated temperature remaining same.



Let the pressure of $\text{PCl}_5 = p$ atm

$$\therefore P_{\text{PCl}_3} = \frac{\alpha}{1+\alpha} \times P, P_{\text{Cl}_2} = \frac{\alpha}{1+\alpha} \times P$$

$$P_{\text{PCl}_5} = \frac{1-\alpha}{1+\alpha} \times P$$

Substituting the values in the relation

$$K_p = \frac{[P_{\text{Cl}_3}][P_{\text{Cl}_2}]}{[P_{\text{PCl}_5}]} = \frac{\left[\frac{\alpha}{1+\alpha} \right] P \left[\frac{\alpha}{1+\alpha} \right] P}{\left[\frac{1-\alpha}{1+\alpha} \right] P} = \frac{\alpha^2 P}{(1-\alpha^2)}$$

When $P = 4$ atm, $\alpha = 10/100 = 0.1$

$$\therefore K_p = \frac{0.1 \times 0.1 \times 4}{1 - (0.1)^2} = \frac{0.04}{0.99} = \frac{4}{99} = 0.04 \text{ atm}$$

Calculation of pressure when $\alpha = 0.2$

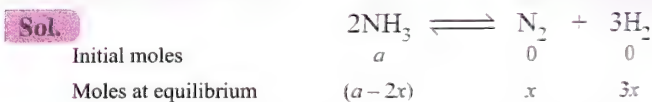
Here $K_p = 0.04$ atm (since temperature is same)

\therefore Substituting the value in the relation,

$$K_p = \frac{\alpha^2 P'}{(1-\alpha^2)} \\ 0.04 = \frac{0.2 \times 0.2 \times P'}{1 - (0.2)^2} \therefore P' = \frac{0.04 \times 0.96}{0.04} = 0.96 \text{ atm}$$

EXAMPLE 7.17

NH_3 is heated at 15 atm from 25°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium of the reaction $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$. Calculate % of moles of NH_3 actually decomposed.



Initial pressure of NH_3 of a moles = 15 atm at 27°C

The pressure of a moles of $\text{NH}_3 = P$ atm at 347°C

$$\therefore 15/300 = P/620$$

$$\therefore P = 31 \text{ atm}$$

At constant volume and at 347°C moles \propto Pressure

$a \propto 31$ before equilibrium

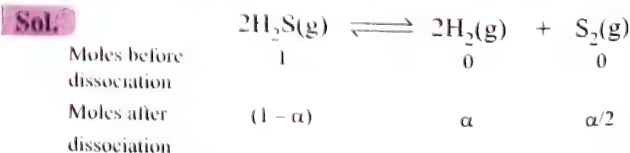
$a + 2x \propto 50$ after equilibrium

$$\therefore \frac{a+2x}{a} = \frac{50}{31} \therefore x = \frac{19}{62} a$$

$$\therefore \% \text{ of } \text{NH}_3 \text{ decomposed} = \frac{2x}{a} \times 100 \\ = \frac{2 \times 19a}{62 \times a} \times 100 = 61.3\%$$

EXAMPLE 7.18

What is the % dissociation of H_2S if 1 mole of H_2S is introduced into a 1.10 L vessel at 1000 K? K_c for the reaction



where α is the degree of dissociation of H_2S .

Volume of container = 1.10 L

$$\therefore K_{c_1} = \frac{[S_2^{2-}]}{[S^{2-}]} = 1.7 \quad \dots(i)$$

$$K_{c_2} = \frac{[S_3^{2-}]}{[S^{2-}]} = 5.3 \quad \dots(ii)$$

Now for $S_2^{-2} + S(s) \rightleftharpoons S_3^{-2}$

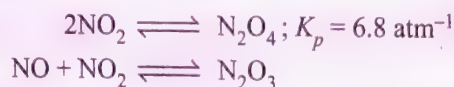
$$K_c = \frac{[S_3^{2-}]}{[S_2^{2-}]}$$

\therefore By dividing equations (ii) by (i),

$$\frac{K_{c_2}}{K_{c_1}} = \frac{[S_3^{2-}]}{[S_2^{2-}]} \Rightarrow K_c = 3.11$$

EXAMPLE 7.25

When NO and NO₂ are mixed, the following equilibria are readily obtained;



In an experiment when NO and NO₂ are mixed in the ratio of 1:2, the final total pressure was 5.05 atm and the partial pressure of N₂O₄ was 1.7 atm. Calculate

a. the equilibrium partial pressure of NO.

b. K_p for $NO + NO_2 \rightleftharpoons N_2O_3$.

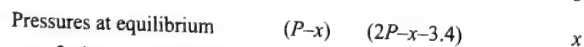
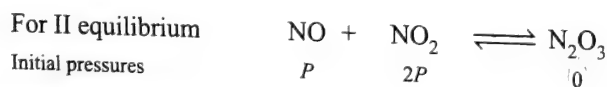
Sol. For I equilibrium $2NO_2 \rightleftharpoons N_2O_4$

$$K_p = \frac{P'_{N_2O_4}}{(P'_{NO_2})^2} = 6.8 \quad \dots(i)$$

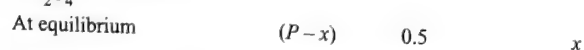
$$P'_{N_2O_4} = 1.7 \text{ atm}$$

\therefore By equation (i), $P'_{NO_2} = 0.5 \text{ atm}$

The equilibria is maintained using NO and NO₂ in the ratio 1 : 2.



\therefore 3.4 atm of NO₂ is used for I equilibrium to have $P'_{N_2O_4} = 1.7 \text{ atm}$



($\because P'_{NO_2}$ is same for both the equilibria since both reactions are at equilibrium at a time)

Total pressure at equilibrium (Given 5.05 atm)

$$= P'_{NO} + P'_{NO_2} + P'_{N_2O_5} + P'_{N_2O_4}$$

$$= P - x + 0.5 + x + 1.7$$

$$\therefore 5.05 = P + 2.20$$

$$\therefore P = 5.05 - 2.20$$

$$\therefore P = 2.85 \text{ atm}$$

$$\therefore 2P - x - 3.4 = 0.5$$

$$2 \times 2.85 - x - 3.4 = 0.5$$

$$\therefore x = 5.70 - 3.90 = 1.80 \text{ atm}$$

$$\therefore P'_{NO} = 2.85 - 1.80 = 1.05 \text{ atm}$$

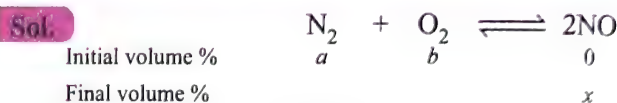
Now K_p for $NO + NO_2 \rightleftharpoons N_2O_3$

$$K_p = \frac{P'_{N_2O_3}}{P'_{NO} \times P'_{NO_2}} = \frac{1.80}{1.05 \times 0.5} = 3.43 \text{ atm}^{-1}$$

EXAMPLE 7.26

N₂ and O₂ combine at a given temperature to produce NO. At equilibrium the yield of NO is 'x' percent by volume. If $x =$

$\sqrt{Ka \cdot b} - \frac{K(a+b)}{4}$, where K is the equilibrium constant of the given reaction at the given temperature and a and b are the volume percentage of N₂ and O₂, respectively, in the initial state. Report the maximum value of K at which X is maximum.



$$\text{Also } x = \sqrt{Ka \cdot b} - \frac{K(a+b)}{4} \quad \dots(i)$$

The x is maximum only when condition of maximum is fulfilled,

$$\text{i.e., } \delta x / \delta a \text{ and } \delta x / \delta b = 0$$

By partial differentiation of x with respect to a keeping b constant.

From equation (i)

$$\frac{\delta x}{\delta a} = \frac{Kb}{2\sqrt{K \cdot a \cdot b}} - \frac{K}{4} = \frac{\sqrt{Kb}}{2\sqrt{a}} - \frac{K}{4} = 0 \quad \dots(ii)$$

By partial differentiation of x wrt b keeping a constant

From equation (i)

$$\frac{\delta x}{\delta b} = \frac{Ka}{2\sqrt{K \cdot a \cdot b}} - \frac{K}{4} = \frac{\sqrt{Ka}}{2\sqrt{b}} - \frac{K}{4} = 0 \quad \dots(iii)$$

By equation (ii), $Kab = 4b^2$

By equation (3), $Kab = 4a^2$

$$\therefore a = b$$

Note: Also this is valid only when $K < 4$, because if $a = b$, Equation (i) yields

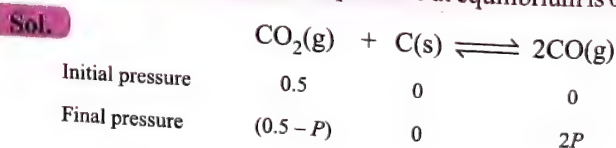
$$x = \sqrt{Ka^2} - \frac{Ka}{2} = \left(\sqrt{K} - \frac{K}{2} \right)$$

If x is (+ve) $\sqrt{K} > K/2$ or $4K > K^2$

$$\text{or } K(4 - K) > 0 \text{ or } 0 < K < 4$$

EXAMPLE 7.27

A vessel at 1000 K contains CO₂ with a pressure of 0.5 atm. Some of the CO₂ is converted into CO on addition of graphite. Calculate the value of K , if total pressure at equilibrium is 0.8 atm.



$$\therefore 0.5 - P + 2P = 0.8$$

$$\therefore P = 0.3 \text{ atm}$$

Therefore, final partial pressures at equilibrium are

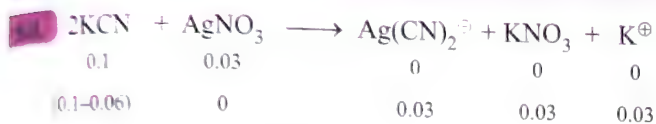
$$P_{\text{CO}_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$

$$P_{\text{CO}} = 2P = 2(0.3) = 0.6 \text{ atm}$$

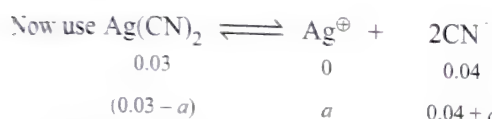
$$K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(0.6)^2}{0.2} = 1.8$$

EXAMPLE 7.28

For the reaction $\text{Ag}(\text{CN})_2^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$, the K_c at 25°C is 4×10^{-19} . Calculate $[\text{Ag}^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in AgNO_3 .



$$\therefore [\text{Ag}(\text{CN})_2^-] = 0.03 \text{ M}$$



Since K_c is too small and dissociation of $\text{Ag}(\text{CN})_2^-$ is very less and thus,

$$\therefore 0.04 + a \approx 0.04 \text{ and } 0.03 - a = 0.03$$

$$\text{Ag}(\text{CN})_2^- = 0.03; [\text{Ag}^+] = a; [\text{CN}^-] = 0.04$$

$$\text{Now, } K_c = \frac{[\text{Ag}^+][\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2^-]} = \frac{a \times (0.04)^2}{0.03}$$

$$\therefore a = 7.5 \times 10^{-18}$$

EXAMPLE 7.29

$\Delta G^\circ = 77.77 \text{ kJ mol}^{-1}$ at 1000 K for the reaction $1/2\text{N}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g})$. What is the partial pressure of NO under equilibrium at 1000 K for air at 1 atm pressure containing 80% N_2 and 20% O_2 by volume.

$$\Delta G^\circ = -2.303 RT \log K_p$$

$$77.77 \times 10^3 = -2.303 \times 8.314 \times 1000 \log K_p$$

$$K_p = 8.67 \times 10^{-5}$$



$$K_c = \frac{[\text{NO}]}{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}$$

$$\therefore 8.67 \times 10^{-5} = \frac{x}{(0.8 - x/2)^{1/2} (0.2 - x/2)^{1/2}}$$

$$x = 3.47 \times 10^{-5} \text{ atm}$$

EXAMPLE 7.30

A saturated aqueous solution of $\text{Mg}(\text{OH})_2$ has a vapour pressure of 759.5 mm at 373 K. Calculate the solubility product of $\text{Mg}(\text{OH})_2$. (Assume molarity equals molality).

Sol. $p_s = 759.5 \text{ mm}$, $P_{\text{H}_2\text{O}} = 760 \text{ mm}$ at 373K

$$\therefore \Delta P = p_s - P_{\text{H}_2\text{O}} = 0.5$$

$$\Delta p/p = 0.5/760 = x_2 = 6.5 \times 10^{-4}$$

We know,

$$\text{Molality } (m) = \frac{\text{moles of solute}}{\text{Volume of solvent (kg)}}$$

$$\therefore m = \frac{x_2 \times 1000}{x_1 \times M_{w_1}} = \frac{(6.5 \times 10^{-4}) \times 1000}{(1 - 6.5 \times 10^{-4}) \times 18} = 0.036$$



$i = 3$ (Assuming 100% ionisation)

$$\text{Solubility } (S) = m/i$$

$$S = 0.036/3 = 0.012 \text{ M}$$

$$K_{\text{SP}} = 4S^3 = 4 \times (0.012)^3 = 6.8 \times 10^{-6}$$

EXAMPLE 7.31

For the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, $K_p = 1.16$ atm at 800°C . If 20.0 g of CaCO_3 was put in to 10 L container and heated to 800°C , what percentage of the CaCO_3 would remain unreacted at equilibrium.

Sol. $\text{CaCO}(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$K_p = P_{\text{CO}_2} = 1.16 \text{ atm}$$

$$n(\text{CO}_2) = \frac{PV}{RT} = \frac{1.16 \text{ atm} \times 10.0 \text{ L}}{(0.0821 \text{ L atm mol}^{-1} \text{K}^{-1})(1073 \text{ K})} = 0.132 \text{ mol}$$

$$\text{Moles of CaCO}_3 \text{ initially present} = 20/100 = 0.2 \text{ mol}$$

$$\% \text{ of dissociation of CaCO}_3 = \frac{0.132}{0.2} \times 100 = 66\%$$

$$\% \text{ of CaCO}_3 \text{ left} = 100 - 66 = 34\%$$

EXAMPLE 7.32

Consider the reaction:



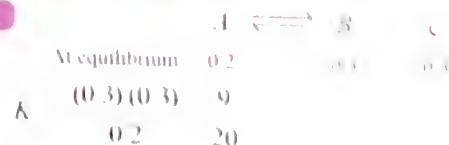
When the system is at equilibrium at 200°C , the concentrations are found to be:

$$[\text{A}] = 0.20 \text{ M}, [\text{B}] = 0.30 \text{ M}, [\text{C}] = 0.30 \text{ M}$$

a. If the volume of the container is suddenly doubled at 200°C , find the equilibrium concentrations.

b. If the volume of the container is suddenly halved (instead of being doubled in part (i) at 200°C , find the equilibrium concentrations.

Sol.



a. When volume is doubled (i.e. $\rightarrow 2V$)

$$[\text{A}] = 0.1, [\text{B}] = 0.15, [\text{C}] = 0.15$$

$$Q = \frac{(0.15)(0.15)}{0.1} = \frac{9}{40} \Rightarrow Q < K$$

Reaction goes forward.

$$K_c = \frac{9}{20} = \frac{(0.15 + x)(0.15 + x)}{(0.1 - x)}$$

Solve for x , $x \approx 0.03$

$$[A] = 0.1 - 0.03 = 0.07 \text{ M}$$

$$[B] = [C] = 0.15 + 0.03 = 0.18 \text{ M}$$

b. When volume is halved (i.e. $V \rightarrow V/2$)

$$\Rightarrow [A] = 0.4, [B] = [C] = 0.6$$

$$Q_c = \frac{0.6 \times 0.6}{0.4} = \frac{9}{10} \Rightarrow Q_c > K_c$$

Reaction goes backward.

$$K_c = \frac{9}{20} = \frac{(0.6 - x)^2}{(0.4 + x)}$$

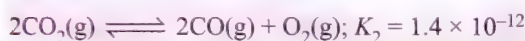
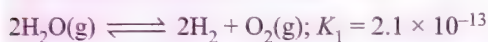
Solve for x , $x \approx 0.12$

$$[A] = 0.4 + 0.12 = 0.16 \text{ M}$$

$$[B] = [C] = 0.6 - 0.12 = 0.48 \text{ M}$$

EXAMPLE 7.33

Calculate the equilibrium constant for the reaction: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ at 1395 K if equilibrium constant at 1395 K are the following:

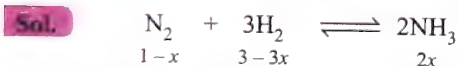


$$\text{Sol. } K = (K_2/K_1)^{1/2} = (1.4 \times 10^{-12}/2.1 \times 10^{-13})^{1/2} \\ = (20/3)^{1/2} = 2.58$$

EXAMPLE 7.34

Calculate the total pressure developed in a vessel containing a mixture of three parts H_2 and one part of N_2 to give a mixture containing 10% ammonia (by moles) at equilibrium at 450°C.

K_p for $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is 1.6×10^{-4} atm units at 450°C



$$\text{Total moles} = 4 - 2x$$

$$[\text{NH}_3] = \frac{2x}{4-2x} = \frac{10}{100} \Rightarrow x = \frac{0.2}{0.1} = \frac{2}{11}$$

$$p_{\text{N}_2} = \frac{(1-x)}{4-2x} P = \frac{0.9P}{4}; p_{\text{H}_2} = \frac{3-3xP}{4-2x} = \frac{2.7P}{4}$$

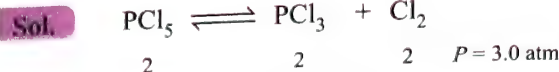
$$p_{\text{NH}_3} = \frac{2x}{4-2x} P = 0.1 P$$

$$\therefore K_p = \frac{(0.1 P)^2}{(0.9 P/4)(2.7 P/4)^3} \Rightarrow P^2 \approx 903,$$

$$\Rightarrow P = 30.03 \text{ atm}$$

EXAMPLE 7.35

A container of volume V L contains an equilibrium mixture that consists of 2 mol each of gaseous PCl_5 , PCl_3 and Cl_2 at 3 atm and T K. Some Cl_2 is added until the volume is double keeping P and T constant. Calculate moles of Cl_2 added and K_p for $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$



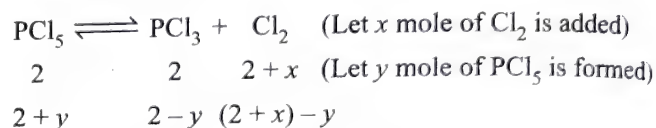
$$\text{Total moles} = 2 + 2 + 2 = 6$$

$$p_{\text{PCl}_5} = 2 \times 3/6 = 1, p_{\text{PCl}_3} = 1, p_{\text{PCl}_2} = 1$$

$$K_p = \frac{(1)(1)}{1} = 1 \text{ atm}$$

When volume is double (i.e., $V \rightarrow 2V$) at constant P and T , total moles become = 12.

If volume is doubled, reaction will move backward at constant P and T .



$$2+y \quad 2-y \quad (2+x)-y$$

$$p_{\text{PCl}_5} = \frac{(2+y)}{12} \times 3, p_{\text{PCl}_3} = \frac{(2-y)}{12} \times 3$$

$$p_{\text{Cl}_2} = \frac{(2+x)-y}{12} \times 3$$

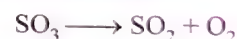
$$\therefore K_p = 1 = \frac{\left(\frac{(2-y)}{12}\right) \times 3 \times \left[\frac{(2+x)-y}{12}\right] \times 3}{\left(\frac{(2+y)}{12}\right) \times 3} \quad \dots(i)$$

$$\text{Also } 2+y+2-y+(2+x)-y = 12 \quad \dots(ii)$$

From equations (i) and (ii), solve, $y = 2/3, x \Rightarrow 20/3$

EXAMPLE 7.36

Consider the following equilibrium:



8.0 g of SO_3 are put in a container at 600°C. The equilibrium pressure and density are 1.8 atm and 1.6 g L⁻¹, respectively.

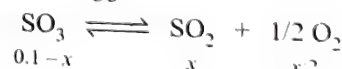
a. Find the value of K_p .

b. Also find the moles of helium that is to be added at equilibrium to double the pressure at constant temperature.

Sol. Weight of SO_3 taken = 8.0 g

Molecular weight of SO_3 = 80 g/mol

$$\therefore \text{mole of } \text{SO}_3 = \frac{8}{80} = 0.1 \text{ mol}$$



$$PV = nRT \text{ or } PM = dRT$$

$$\text{Total moles} = 0.1 + x/2$$

$$\Rightarrow M = \frac{dRT}{P} = \frac{1.6 \times 0.0821 \times 873}{1.8} = 63.6$$

$$n_1 M_1 = n_2 M_2; \frac{n_1}{n_2} = \frac{M_2}{M_1}$$

$$\Rightarrow \frac{0.1}{0.1 + x/2} = \frac{M_{\text{av}}}{M_{\text{SO}_3}} = \frac{63.6}{80} \Rightarrow x = 0.05$$

$$\therefore K_p = \frac{\left(\frac{x/2}{0.1 + x/2} P\right)^{1/2} \left(\frac{x P}{0.1 + x/2}\right)}{\left(\frac{0.1 - x}{0.1 + x/2} P\right)} = 0.61$$

$$(P = 1.8 \text{ atm})$$

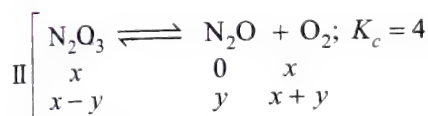
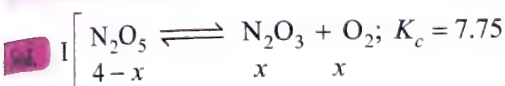
$$\text{b. } n_i = 0.1 \text{ } x/2$$

To double pressure by adding inert gas at constant T double moles at equilibrium $\Rightarrow n_f = 2(0.1 + x/2)$

$$\Rightarrow n_{\text{He added}} = 0.1 + x/2 = 0.1 + (0.05/2) = 0.125$$

EXAMPLE 7.37

When $\text{N}_2\text{O}_5(\text{g})$ is heated it dissociates to give N_2O_3 and O_2 . K_c for $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_3 + \text{O}_2$ is 7.75 and K_c for $\text{N}_2\text{O}_3 \rightarrow \text{N}_2\text{O} + \text{O}_2$ is 4.0 mol L^{-1} . (both K_c are at same temperature) 4 mol N_2O_5 in 1.0 L vessel is kept at a certain temperature. The concentration of O_2 was 4.5 mol L^{-1} . Find the concentration of N_2O_5 , N_2O_3 , and N_2O at equilibrium.



$$\therefore x+y = [\text{O}_2] = 4.5$$

$$\text{From I, } K_c = \frac{[\text{N}_2\text{O}_3][\text{O}_2]}{[\text{N}_2\text{O}_5]}$$

$$7.75 = \frac{[\text{N}_2\text{O}_3][\text{O}_2]}{[\text{N}_2\text{O}_5]} = \frac{(x-y)(4.5)}{4-x}$$

$$\text{From II, } K_c = \frac{[\text{N}_2\text{O}][\text{O}_2]}{[\text{N}_2\text{O}_3]} = 4 = \frac{y \times (4.5)}{x-y}$$

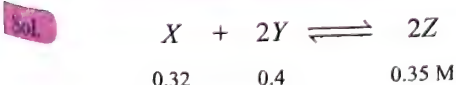
$$\text{Solve to find } x \text{ and } y [x = 3.06, y = 1.44].$$

EXAMPLE 7.38

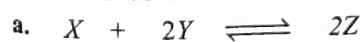
For a reversible reaction: $X + 2Y \rightarrow 2Z$, the equilibrium concentrations of X , Y and Z are 0.32, 0.40 and 0.35 moles L^{-1} respectively at 25°C .

a. If initially the system contained only X and Y and then reached the state of equilibrium, what were the initial concentrations of X and Y .

b. If at the start only X and Z were present, what were the initial concentrations?



$$\Rightarrow K = \frac{[Z]^2}{[X][Y]^2} = 2.392$$



$$\begin{array}{ccc} a & b & - \\ a-x & b-2x & 2x \end{array}$$

$$\Rightarrow 2x = 0.35 \Rightarrow x = 0.175$$

$$\Rightarrow a = [X]_0 = x + 0.32 = 0.495 \text{ M}$$

$$b = [Y]_0 = 2x + 0.4 = 0.75 \text{ M}$$

b. Since we start with X and Z

\Rightarrow 'Z' will decomposes to produce $X + Y$.



$$\begin{array}{ccc} p & q & \\ P-y & q+y/2 & y \end{array}$$

$$\Rightarrow y = 0.4 \text{ M}$$

$$P = [Z] = 0.35 + y = 0.75 \text{ M}$$

$$q = [X] = 0.33 - y/2 = 0.12 \text{ M}$$

EXAMPLE 7.39

Under what pressure conditions $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ be efforescent at 35°C . How good a drying agent is $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ at the same temperature? Given



$K_p = 1.268 \times 10^{-3} \text{ atm}^2$ at 35°C . Vapour pressure of water at 35°C is 25.0 mm Hg.

Sol. An efforescent salt is one that loses H_2O to atmosphere for the reaction,

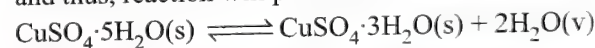


$$K_p = (P'_{\text{H}_2\text{O}})^2 = 1.268 \times 10^{-3}$$

$$\therefore P'_{\text{H}_2\text{O}} = 0.0356 \text{ atm} = 27.0 \text{ mm Hg}$$

\therefore Given $P'_{\text{H}_2\text{O}}$ at 35°C , (i.e., 25.0 mm Hg) $< 27.0 \text{ mm Hg}$

and thus, reaction will proceed in forward direction, i.e.,



Thus, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will acts as efflorescent

EXAMPLE 7.40

Under what pressure conditions $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ be efforescent at 25°C . How good a drying agent is $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ at the same temperature? Given



$K_p = 1.086 \times 10^{-4} \text{ atm}^2$ at 25°C . Vapour pressure of water at 25°C is 23.8 mm of Hg.

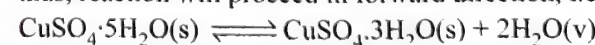
Sol. An efforescent salt is one that loses H_2O to atmosphere for the reaction,



$$K_p = (P'_{\text{H}_2\text{O}})^2 = 1.086 \times 10^{-4}$$

$$\therefore P'_{\text{H}_2\text{O}} = 1.042 \times 10^{-2} \text{ atm} = 7.92 \text{ mm}$$

\therefore Given $P'_{\text{H}_2\text{O}}$ at 25°C , (i.e., 23.8 mm Hg) $< 7.92 \text{ mm}$ and thus, reaction will proceed in forward direction, i.e.,



Thus, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will acts as efflorescent but on the contrary $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ will absorb moisture from the atmosphere under given conditions. The salt $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will effloresce only on a dry day when the aqueous tension or partial pressure of moisture in the air is lesser than 7.92 mm

$$\text{of relative humidity of air at } 25^\circ\text{C} = \frac{7.92}{23.8} = 0.333 \text{ or } 33.3\%$$

EXAMPLE 7.41

From the data given below derive which of the following reactant is most effective drying agent at 0°C . Given $P_{\text{H}_2\text{O}}^\circ = 4.58 \text{ mm}$ at 0°C .

- $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{g});$
 $K_p = 6.9 \times 10^{-12} \text{ atm}^4$
- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Na}_2\text{SO}_4(\text{s}) + 10\text{H}_2\text{O}(\text{g});$
 $K_p = 4.08 \times 10^{-25} \text{ atm}^{10}$
- $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 5\text{H}_2\text{O}(\text{g});$
 $K_p = 5.25 \times 10^{-13} \text{ atm}^5$

Sol. For (i) $K_p = (P_{\text{H}_2\text{O}})^4$

$$\therefore P_{\text{H}_2\text{O}} = \sqrt[4]{K_p} = \sqrt[4]{6.9 \times 10^{-12}} = 1.62 \times 10^{-3} \text{ atm}$$

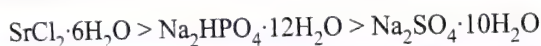
For (ii) $K_p = (P_{\text{H}_2\text{O}})^{10}$

$$P_{\text{H}_2\text{O}} = \sqrt[10]{K_p} = \sqrt[10]{4.08 \times 10^{-25}} = 3.64 \times 10^{-3} \text{ atm}$$

For (iii) $K_p = (P_{\text{H}_2\text{O}})^5$

$$\therefore P_{\text{H}_2\text{O}} = \sqrt[5]{K_p} = \sqrt[5]{5.25 \times 10^{-13}} = 3.5 \times 10^{-3} \text{ atm}$$

All these reactant can be used as drying agent since their $P_{\text{H}_2\text{O}}$ is lesser than V.P. of H_2O in atmosphere, i.e., 4.58 mm or $6.02 \times 10^{-3} \text{ atm}$. The efficiency order is

**EXAMPLE 7.42**

Following two equilibria are established on mixing two gases A_2 and C .

- $3\text{A}_2(\text{g}) \rightleftharpoons \text{A}_6(\text{g}) \quad K_p = 1.6 \text{ atm}^{-2}$
- $\text{A}_2(\text{g}) + \text{C}(\text{g}) \rightleftharpoons \text{A}_2\text{C}(\text{g})$

If A_2 and C are mixed in 2 : 1 molar, ratio, calculate the equilibrium partial pressures of A_2 , C , A_2C and K_p for the reaction (ii). Given that the total pressure to be 1.4 atm and partial pressure of A_6 to be 0.2 atm at equilibrium

Sol. $3\text{A}_2(\text{g}) \rightleftharpoons \text{A}_6(\text{g})$

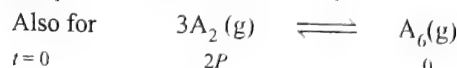
$$K_p = 1.6 = \frac{P_{\text{A}_6}}{(P_{\text{A}_2})^3}$$

$$P_{\text{A}_2} = \sqrt[3]{\frac{0.2}{16}} = 0.5 \text{ atm}$$

Also pressure of A_2 used for the formation of $\text{A}_6 = 0.6 \text{ atm}$



$$\begin{array}{ccc} t=0 & 2P & P & 0 \\ \text{At Eq} & 2P - P' - 0.6 & P - P' & P' \end{array}$$



$$\begin{array}{ccc} t=0 & 2P & 0 \\ \text{At Eq} & 2P - P' - 0.6 & 0.2 \end{array}$$

(since P_{A_2} at equilibrium is 0.5 for simultaneous equilibria)

Also pressure of $\text{A}_2 + \text{C} + \text{A}_2\text{C} + \text{A}_6$

$$= (2P - P' - 0.6) + (P - P') + P' + 0.2 = 1.4$$

$$0.5 + P + 0.2 = 1.4$$

$$P = 0.7 \text{ atm}$$

$$\therefore 2P - P' - 0.6 = 0.5$$

$$\therefore P' = 2 \times 0.7 - 0.6 - 0.5$$

$$P' = 0.3 \text{ atm}$$

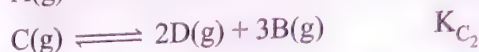
$$\therefore P_{\text{A}_2} = 0.5 \text{ atm}, P_{\text{C}} = 0.7 - 0.3 = 0.4 \text{ atm}, P_{\text{A}_2\text{C}} = 0.3 \text{ atm}$$

Also K_p for $\text{A}_2(\text{g}) + \text{C}(\text{g}) \rightleftharpoons \text{A}_2\text{C}(\text{g})$

$$K_p = \frac{P_{\text{A}_2\text{C}}}{P_{\text{A}_2} \times P_{\text{C}}} = \frac{0.3}{0.5 \times 0.4} = 1.5 \text{ atm}^{-1}$$

EXAMPLE 7.43

1 mol of A in 1 litre vessel maintained at constant T shows the equilibrium



If the equilibrium pressure is $\frac{13}{6}$ times of initial pressure and

$[\text{C}]_{\text{eq}} = \frac{4}{9} [\text{A}]_{\text{eq}}$, Calculate K_{C_1} and K_{C_2} .

Sol. $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + 2\text{C}(\text{g})$ and $\text{C} \rightleftharpoons 2\text{D} + 3\text{B}(\text{g})$

$$\begin{array}{ccccccc} 1 & & 0 & 0 & & & \\ 1-a & (a+3b) & 2a-b & 2a-b & 2b & (a+3b) & \end{array}$$

$$\therefore \Sigma \text{ mole at equilibrium} = 1 - a + a + 3b + 2a - b + 2b = 2a + 4b + 1$$

Now, $P_{\text{initial}} \propto 1$

$$P_{\text{eq}} \propto 2a + 4b + 1$$

$$\therefore 2a + 4b + 1 = \frac{13}{6}$$

$$\text{or } 2a + 4b = \frac{7}{6} \quad \dots(\text{i})$$

$$\text{Also } [\text{C}]_{\text{eq}} = \frac{4}{9} [\text{A}]_{\text{eq}}$$

$$2a - b = \frac{4}{9} \times (1 - a)$$

$$22a - 9b = 4$$

By equations (i) and (ii) $a = 0.25$, $b = 0.167$

$$\begin{aligned} \therefore K_{\text{C}_1} &= \frac{[\text{B}][\text{C}]^2}{[\text{A}]} = \frac{(a+3b)(2a-b)^2}{(1-a)} \\ &= \frac{[0.25 + (3 \times 0.167)][0.5 - 0.167]^2}{(1 - 0.25)} = 0.11 \end{aligned}$$

$$\begin{aligned} \therefore K_{\text{C}_2} &= \frac{[\text{D}]^2 [\text{B}]^2}{[\text{C}]} = \frac{(2b)^2 (a+3b)^3}{(2a-b)} \\ &= \frac{[2 \times 0.167]^2 [0.25 + (3 \times 0.167)]^3}{[0.5 - 0.167]} = 0.142 \end{aligned}$$

EXAMPLE 7.44

One mole of $\text{N}_2\text{O}_4(\text{g})$ at 100 K is kept in a closed container at 1.0 atm pressure. It is heated to 400 K , where 30% by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. The resultant pressure will be

- a. 4.2 b. 5.2 c. 3.2 d. 6.2

Sol. b. Since volume is constant. Therefore on increasing the temperature four times, Pressure becomes four times

$$\therefore P = 4 \text{ atm}$$

Decomposition of N_2O_4 30% by mass \propto 30% by mole

$$\therefore \alpha = \frac{30}{100} = 0.3$$

	N_2O_4	\rightleftharpoons	2NO_2
Initial	1		0
At. equilibrium	$1 - 0.3$		2×0.3
	$= 0.7$		$= 0.6$

$$\text{Total moles} = 0.7 + 0.6 = 1.3$$

$$\frac{\text{Initial mole}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure after change of temperature}}{\text{Equilibrium pressure}}$$

$$\frac{1}{1.3} = \frac{4}{P} \Rightarrow P = 5.2 \text{ atm}$$

Alternate method:

$$\alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

$$0.3 = \frac{100 \times P_2 - 400 \times 1}{400 \times 1}$$

$$\Rightarrow P_2 = 5.2 \text{ atm}$$

Exercises

Single Correct Answer Type

1. In the dissociation of
- PCl_5
- as

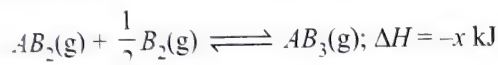


if the degree of dissociation is α at equilibrium pressure P , then the equilibrium constant for the reaction is

$$(1) K_p = \frac{\alpha^2}{1 + \alpha^2 P} \quad (2) K_p = \frac{\alpha^2 P^2}{1 - \alpha^2}$$

$$(3) K_p = \frac{P^2}{1 - \alpha^2} \quad (4) K_p = \frac{\alpha^2 P}{1 - \alpha^2}$$

2. For a hypothetical reaction of the kind



More AB_3 could be produced at equilibrium by

- (1) Using a catalyst (2) Removing some of B_2
(3) Increasing the temperature (4) Increasing the pressure

3. The equilibrium constant for a reaction,

$A + B \rightleftharpoons C + D$ is 1.0×10^{-2} at 298 and is 2.0 at 373 K. The chemical process resulting in the formation of C and D is

- (1) Exothermic (2) Endothermic
(3) Unpredictable (4) None

4. The solubility of
- CO_2
- in water increases with

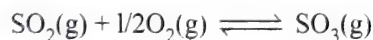
- (1) Increase in temperature (2) Reduction of gas pressure
(3) Increase in gas pressure (4) Increase in volume

5. The equilibrium constant for a reaction

$A + 2B \rightleftharpoons 2C$ is 40. The equilibrium constant for reaction $C \rightleftharpoons B + 1/2 A$ is

- (1) $1/40$ (2) $(1/40)^{1/2}$ (3) $(1/40)^2$ (4) 40

6. Inert gas has been added to the following equilibrium system at constant volume



To which direction will the equilibrium shift?

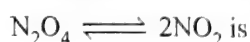
- (1) Forward (2) Backward
(3) No effect (4) Unpredictable

7. The equilibrium constant
- K
- for the reaction:

$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ at room temp is 2.85 and that at 698 K is 1.4×10^{-2} . This implies that the forward reaction is

- (1) Exothermic (2) Endothermic
(3) Exergonic (4) Unpredictable

8. The decomposition of
- N_2O_4
- to
- NO_2
- is carried out at
- 280°C
- in chloroform. When equilibrium is reached, 0.2 mol of
- N_2O_4
- and
- 2×10^{-3}
- mol of
- NO_2
- are present in a 2L solution. The equilibrium constant for the reaction



- (1) 1×10^{-2} (2) 2×10^{-3} (3) 1×10^{-5} (4) 2×10^{-5}

9. For the reaction
- $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- , the degree of dissociation at equilibrium is 0.2 at 1 atm pressure. The equilibrium constant
- K_p
- will be

- (1) $1/2$ (2) $1/4$ (3) $1/6$ (4) $1/8$

10. 4 mol of carbon dioxide was heated in
- 1 dm^3
- vessel under conditions which produced at equilibrium 25% dissociation into carbon monoxide and oxygen. The number of moles of carbon monoxide produced

- (1) 0.5 (2) 1.0 (3) 2.0 (4) 4.0

11. 1 mol of
- N_2
- is mixed with 3 mol of
- H_2
- in a litre container. If 50% of
- N_2
- is converted into ammonia by the reaction
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- , then the total number of moles of gas at the equilibrium are

- (1) 1.5 (2) 4.5 (3) 3.0 (4) 6.0

12. The equilibrium constant of a reaction is 300, if the volume of the reaction flask is tripled, the equilibrium constant will be

- (1) 100 (2) 300 (3) 250 (4) 150

13. For a reaction:
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- at certain temperature, the value of equilibrium constant is 50. If the volume of the vessel is reduced to half of its original volume, the value of new equilibrium constant will be

- (1) 25 (2) 50
(3) 100 (4) Unpredictable

14. The system
- $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- attains equilibrium. If the equilibrium concentration of
- $\text{PCl}_3(\text{g})$
- is doubled, the concentration of
- $\text{Cl}_2(\text{g})$
- would become

- (1) $1/4$ its original value (2) $1/2$ its original value
(3) Twice its original value (4) Unpredictable

- 15.
- XY_2
- dissociates
- $\text{XY}_2(\text{g}) \rightleftharpoons \text{XY}(\text{g}) + \text{Y}(\text{g})$
- . When the initial pressure of
- XY_2
- is 600 mm Hg, the total equilibrium pressure is 800 mm Hg. Calculate
- K
- for the reaction. Assuming that the volume of the system remains unchanged.

- (1) 50.0 (2) 100.0 (3) 166.6 (4) 400.0

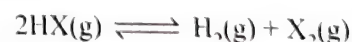
16. Consider the reaction



Which occurs in one step The specific rate constant are 0.25 and 5000 for the forward and reverse reaction, respectively. The equilibrium constant is

- (1) 2.0×10^{-4} (2) 4.0×10^{-2}
(3) 5.0×10^{-5} (4) 2.5×10^{-6}

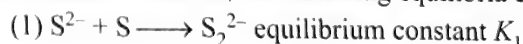
17. For the equilibrium system



the equilibrium constant is 1.0×10^{-5} . What is the concentration of HX if the equilibrium concentration of H_2 and X_2 are $1.2 \times 10^{-3} \text{ M}$, and $1.2 \times 10^{-4} \text{ M}$ respectively?

- (1) $12 \times 10^{-4} \text{ M}$ (2) $12 \times 10^{-3} \text{ M}$
(3) $12 \times 10^{-2} \text{ M}$ (4) $12 \times 10^{-1} \text{ M}$

18. In alkaline solution, the following equilibria exist



- (2) $S_2^{2-} + S \longrightarrow S_3^{2-}$ equilibrium constant K_2
 K_1 and K_2 have values 12 and 11, respectively.
 $S_3^{2-} \longrightarrow S^{2-} + 2S$. What is equilibrium constant for the reaction
- (1) 132 (2) 7.58×10^{-3}
 (3) 1.09 (4) 0.918
19. Given the equilibrium constants
 $HgCl^{\oplus} + Cl^{\ominus} \longrightarrow HgCl_2$, $K_1 = 3 \times 10^6$
 $HgCl_2 + Cl^{\ominus} \longrightarrow HgCl_3^{\ominus}$, $K_2 = 8.9$
 The equilibrium constant for the disproportionation equilibrium
 $2HgCl_2 \longrightarrow HgCl^{\oplus} + HgCl_3^{\ominus}$ is
- (1) -3.3×10^5 (2) 3×10^{-5}
 (3) 3.3×10^5 (4) 3×10^{-6}
20. When the reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$ reaches equilibrium at 298 K. The partial pressure of NO_2 and N_2O_4 are 0.2 KPa and 0.4 KPa, respectively. What is the equilibrium constant K_p of the above reaction at 298 K?
- (1) 0.1 (2) 0.5 (3) 1.0 (4) 10
21. The vapour density of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 275 K. The number of moles of NO_2 in the mixture:
- (1) 0.2 (2) 0.4 (3) 0.8 (4) 1.6
22. In the problem number 21, the number of mole of N_2O_4 in 100 g of the mixture is:
- (1) 0.43 (2) 0.86 (3) 0.57 (4) 0.2
23. One mole of SO_3 was placed in a litre reaction flask at a given temperature when the reaction equilibrium was established in the reaction.
 $2SO_3 \rightleftharpoons 2SO_2 + O_2$ the vessel was found to contain 0.6 mol of SO_2 . The value of the equilibrium constant is
- (1) 0.36 (2) 0.675 (3) 0.45 (4) 0.54
24. The equilibrium constant for the reaction $w + x \rightleftharpoons y + z$ is 9. If one mole of each of w and x are mixed and there is no change in volume, the number of moles of y for formed is
- (1) 0.10 (2) 0.50 (3) 0.75 (4) 0.54
25. In the gaseous equilibrium
 $A + 2B \rightleftharpoons C + \text{Heat}$, the forward reaction is favoured:
- (1) Low P , High T (2) Low P , Low T
 (3) High P , Low T (4) High P , High T
26. The active mass of 64 g of HI in a 2-L flask would be
- (1) 2 (2) 1 (3) 5 (4) 0.25
27. For $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{Heat}$
 (1) $K_p = K_c$ (2) $K_p = K_c RT$
 (3) $K_p = K_c (RT)^{-2}$ (4) $K_p = K_c (RT)^{-1}$
28. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with
- (1) Total pressure

(2) Catalyst

(3) The amounts of H_2 and I_2 present

(4) Temperature

29. The equilibrium constant K for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ at room temperature is 2.85 and that at 698 K is 1.4×10^{-2} . This implies

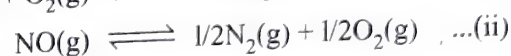
(1) HI is exothermic compound.

(2) HI is very stable at room temperature.

(3) HI is relatively less stable than H_2 and I_2 .

(4) HI is resonance stabilised.

30. K_1 and K_2 are equilibrium constants for reaction (i) and (ii)



Then,

(1) $K_1 = (1/K_2)^2$

(2) $K_1 = K_2^2$

(3) $K_1 = 1/K_2$

(4) $K_1 = (K_2)^0$

31. The equilibrium constant K_p for a homogeneous gaseous reaction is 10^{-8} . The standard Gibbs free energy change ΔG^\ominus for the reaction (using $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) is

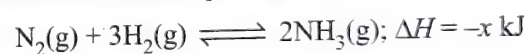
(1) 10.98 kcal

(2) -1.8 kcal

(3) -4.1454 kcal

(4) +4.1454 kcal

32. Which of the following will not change the concentration of ammonia in the equilibrium



(1) increase of pressure

(2) increase of temperature

(3) decrease of volume

(4) addition of catalyst

33. In a chemical reaction, equilibrium is said to have been established when the

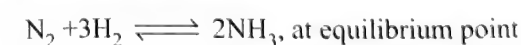
(1) Concentration of reactants and products are equal.

(2) Opposing reaction ceases.

(3) Velocities of opposing reaction become equal.

(4) Temperature of opposing reaction are equal.

34. In a chemical reaction

(1) Equal volumes of N_2 and H_2 are reacting.(2) Equal masses of N_2 and H_2 are reacting.

(3) The reaction has stopped.

(4) The same amount of ammonia is formed as is decomposed into N_2 and H_2 .

35. The equilibrium constant in a reversible reaction at a given temperature which

(1) Depends on initial concentration, of the reactants.

(2) Depends on the concentration of the products at equilibrium.

- (3) Does not depend on the initial concentration.
 (4) It is not characteristic of the reaction.
36. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the
 (1) Amount of solid to decrease.
 (2) Amount of liquid to decrease.
 (3) Temperature to rise.
 (4) Temperature to fall.
37. In the formation of nitric acid, N_2 and O_2 are made to combine. Thus, $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} + \text{Heat}$ which of the following condition will favour the formation of NO?
 (1) low temperature (2) high temperature
 (3) freezing point (4) all are favourable
38. Which of the following factors will favour the reverse reaction in a chemical equilibrium?
 (1) increase in concentration of one of the reactants
 (2) increase in concentration of one of the products
 (3) removal of one of the products regularly
 (4) none of these
39. For the system $\text{A(g)} + 2\text{B(g)} \rightleftharpoons \text{C(g)}$ the equilibrium concentration is
 $\text{A} = 0.06 \text{ mol L}^{-1}$; $\text{B} = 0.12 \text{ mol L}^{-1}$
 $\text{C} = 0.216 \text{ mol L}^{-1}$ The K_{eq} for the reaction is
 (1) 250 (2) 416 (3) 4×10^{-3} (4) 125
40. 4 moles of A are mixed with 4 moles of B, when 2 moles of C are formed at equilibrium according to the reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$.
 The value of equilibrium constant is
 (1) 4 (2) 1 (3) 1/2 (4) 1/4
41. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ in closed container at equilibrium. What would be the effect of addition of CaCO_3 on the equilibrium concentration of CO_2 .
 (1) Increases (2) Decreases
 (3) Data is not sufficient (4) Remains unaffected
42. The equilibrium constant for a reaction
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ is 4×10^{-4} at 2000 K. In the presence of catalyst, the equilibrium constant is attained 10 times faster. The equilibrium constant in the presence of catalyst, at 2000 K is
 (1) 40×10^{-4} (2) 4×10^{-4}
 (3) 4×10^{-2} (4) incomplete data
43. In which of the following reaction, the yield of the products does not increase by increase in the pressure?
 (1) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 (2) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
 (3) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (4) $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$
44. At certain temperature 50% of HI is dissociated into H_2 and I_2 , the equilibrium constant is
 (1) 1.0 (2) 3.0
 (3) 0.5 (4) 0.25
45. For a reaction $\text{A(g)} \rightleftharpoons \text{B(g)} + \text{C(g)}$. K_p at 400°C is 1.5×10^{-4} and K_p at 600°C is 6×10^{-3} . Which statement is incorrect?
 (1) The reaction is exothermic.
 (2) Increase in temperature increases the formation of B.
 (3) Increase in pressure increases the formation of A.
 (4) Decrease in temperature and increase in pressure shift the equilibrium towards left.
46. 8 mol of a gas AB_3 are introduced into a 1.0 dm^3 vessel. It dissociates as $2\text{AB}_3(\text{g}) \rightleftharpoons \text{A}_2(\text{g}) + 3\text{B}_2(\text{g})$
 At equilibrium, 2 mol of A_2 is found to be present. The equilibrium constant for the reaction is
 (1) $2 \text{ mol}^2 \text{ L}^{-2}$ (2) $3 \text{ mol}^2 \text{ L}^{-2}$
 (3) $27 \text{ mol}^2 \text{ L}^{-2}$ (4) $36 \text{ mol}^2 \text{ L}^{-2}$
47. 1 mol of XY(g) and 0.2 mol of Y(g) are mixed in 1 L vessel. At equilibrium, 0.6 mol of Y(g) is present. The value of K for the reaction
 $\text{XY(g)} \rightleftharpoons \text{X(g)} + \text{Y(g)}$ is
 (1) 0.04 mol L^{-1} (2) 0.06 mol L^{-1}
 (3) 0.36 mol L^{-1} (4) 0.40 mol L^{-1}
48. How will the lowering of temperature affect the chemical equilibrium in the system
 $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$, $\Delta H < 0$
 (1) Relative concentration of products and reactants does not change.
 (2) Relative concentration of products and reactants change.
 (3) Equilibrium is shifted to the left.
 (4) Equilibrium is shifted to the right.
49. For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, the value of K_p is 1.7×10^3 at 500 K and 1.7×10^4 at 600 K. Which of the following is/are correct?
 (1) The proportions of NO_2 in the equilibrium mixture is increased by decrease in pressure.
 (2) The standard enthalpy change for the forward reaction is negative.
 (3) Units of K_p are atm^{-1} .
 (4) At 500 K the degree of dissociation of N_2O_4 decreases by 50% by increasing the pressure by 100%.
50. At equilibrium $\text{X} + \text{Y} \rightleftharpoons 3\text{Z}$, 1 mol of X, 2 mol of Y and 4 mol of Z are contained in a 3-L vessel. Among the given values of reaction coefficient Q, given at three different instants, which value refers to system at equilibrium?

Multiple Correct Answers Type

- (1) 10 (2) 15
(3) 10.67 (4) 25
51. What concentration of CO_2 be in equilibrium with 0.025 M CO at 120°C for the reaction



if the value of $K_c = 5.0$?

- (1) 0.125 M (2) 0.0125 M
(3) 1.25 M (4) 12.5 M
52. Which of the following reactions will not be affected by increasing the pressure?

- (1) $\text{PCl}_5\text{(g)} \rightleftharpoons \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$
(2) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$
(3) $\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$
(4) $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$

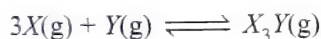
53. For the reaction



at a given temperature, the equilibrium amount of $\text{CO}_2\text{(g)}$ can be increased by

- (1) Adding a suitable catalyst
(2) Adding an inert gas
(3) Decreasing the volume of the container
(4) Increasing the amount of CO(g)

54. For the chemical reaction



The amount of X_3Y at equilibrium is affected by

- 1) Temperature and pressure
2) Temperature only
3) Pressure only
4) Temperature, pressure, and catalyst

55. When two reactants A and B are mixed to give products C and D, the reaction quotient Q at the initial stages of the reaction

- (1) Is zero
(2) Decreases with time
(3) Is independent of time
(4) Increases with time

56. A constant temperature, the equilibrium constant (K_p) for the decomposition reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is expressed by $K_p = (4x^2p)/(1-x^2)$, where p = pressure and x = extent of decomposition. Which one of the following statements is true?

- (1) K_p increases with increase in p
(2) K_p increases with increase in x
(3) K_p increases with decrease in x
(4) K_p remains constant with change in p and x .

1. For the reaction $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$, which of the following factors will have no effect on the value of equilibrium constant?

- (1) Temperature (2) Initial concentration of N_2O_4
(3) Presence of catalyst (4) Pressure

2. For the reaction $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$, the equilibrium can be shifted in favour of product by

- (1) Increasing the $[\text{H}_2]$ (2) Increasing the pressure
(3) Increasing the $[\text{I}_2]$ (4) By using the catalyst

3. A reaction $\text{S}_8\text{(g)} \rightleftharpoons 4\text{S}_2\text{(g)}$ is carried out by taking 2 mol of $\text{S}_8\text{(g)}$ and 0.2 mol of $\text{S}_2\text{(g)}$ is a reaction vessel of 1 L. Which one is not correct if $K_c = 6.30 \times 10^{-6}$

- (1) Reaction quotient is 8×10^{-4}
(2) Reaction proceed in backward direction.
(3) Reaction proceed is forward direction
(4) $K_p = 2.55 \text{ atm}^3$

4. For the equilibrium at 298 K; $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$:
 $G_{\text{N}_2\text{O}_4}^\ominus = 100 \text{ kJ mol}^{-1}$ and $G_{\text{NO}_2}^\ominus = 50 \text{ kJ mol}^{-1}$. If 5 mol of N_2O_4 and 2 moles of NO_2 are taken initially in one litre container than which statement are correct.

- (1) reaction proceeds in forward direction
(2) $K_c = 1$
(3) $\Delta G = -0.55 \text{ KJ}$, $\Delta G^\ominus = 0$
(4) At equilibrium $[\text{N}_2\text{O}_4] = 4.84 \text{ M}$ and $[\text{NO}_2] = 0.212 \text{ M}$

5. Which are true for the reaction: $\text{A}_2 \rightleftharpoons 2\text{C} + \text{D}$?

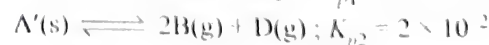
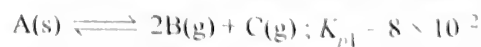
- (1) if $\Delta H = 0$; K_p and increases with temperature and dissociation temperature.
(2) if $\Delta H = +\text{ve}$, K_p increases with temperature and dissociation of A_2 increases.
(3) if $\Delta H = -\text{ve}$; K_p decreases with temperature and dissociation of A_2 decreases.

$$(4) K_p = 4\alpha^3 \left[\frac{P}{1+2\alpha} \right]^2$$

6. van't Hoff equation is

- (1) $(d/dT) \ln K = -\Delta H/RT^2$ (2) $d/dT (\ln K) = +\Delta H/RT^2$
(3) $(d/dT) \ln K = -\Delta H/RT$ (4) $K = Ae^{-\Delta H/RT}$

7. For given two equilibria attained in a container which are correct if degree of dissociation of A and A' are α and α' .



$$(1) \frac{K_{p1}}{K_{p2}} = \left[\frac{(3\alpha' + 2\alpha)}{(3\alpha + 2\alpha')} \right]^3 \times \frac{\alpha}{\alpha'}$$

$$(2) P'_C/P_D = 4$$

$$(3) P'_B = 2P'_C + 2P'_D$$

$$(4) \alpha > \alpha'$$

8. In a reaction $A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g)$, $\Delta H < 0$. The formation of AB_4 is not favoured by

- (1) Low temperature and high pressure
- (2) High temperature and low pressure
- (3) Low temperature and low pressure
- (4) High temperature and high pressure

9. The reaction which proceeds in the backward direction is

- (1) $Fe_3O_4 + 6HCl = 2FeCl_3 + 3H_2O$
- (2) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$
- (3) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2HgCl_2$
- (4) $2CuI + I_2 + 4K^{\oplus} = 2Cu^{2+} + 4KI$

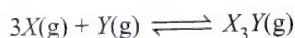
10. For which of the following reaction, $K_p \neq K_c$?

- (1) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
- (2) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- (3) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
- (4) $2N_2O_4(g) \rightleftharpoons 2NO_2(g)$

11. Select the incorrect statements:

- (1) K_p or K_c are dimensionless if pressure or concentration are expressed in standard state.
- (2) The numerical value of K_p changes with experimental conditions, i.e., P , T , and C at which equilibrium is attained.
- (3) Active mass of reactant = concentration of reactant
- (4) Dissolution of NH_3 in water increases with increasing pressure.

12. For the chemical reaction



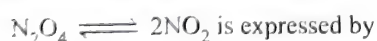
the amount of X_3Y at equilibrium is not affected by

- (1) Temperature and pressure
- (2) Temperature only
- (3) Pressure only
- (4) Temperature, pressure, and catalyst

13. When two reactants A and B are mixed to give products C and D , the reaction quotient, Q , at the initial stages of the reaction

- (1) Is zero
- (2) Decreases with time
- (3) Is independent of time
- (4) Increases with time

14. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction



is expressed by $K_p = (4x^2P)/(1-x^2)$, where P = pressure and x = extent of decomposition. Which one of the following statements is false?

- (1) K_p increases with increase of P
- (2) K_p increases with increases of x
- (3) K_p increases with decrease of x
- (4) K_p remains constant with change in P and x

15. Consider the following equilibrium in a closed container:



At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements, holds false regarding the equilibrium constant (K_p) and degree of dissociation (α)?

- (1) neither K_p nor α changes
- (2) both K_p and α change
- (3) K_p changes but α does not change
- (4) K_p does not change but α changes

16. Which of the following do not change the value of K for a reaction?

- (1) Addition of catalyst
- (2) Increase in temperature
- (3) Increase in pressure
- (4) Removal of one of the products

17. For which of the following reactions at equilibrium at constant temperature, doubling the volume will cause a shift to the right?

- (1) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- (2) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- (3) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
- (4) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

18. Unit of equilibrium constant is:

- (1) $(\text{mol L}^{-1})^{1-n}$
- (2) $(\text{mol L}^{-1})^{\Delta n}$
- (3) $(\text{atm})^{\Delta n}$
- (4) All

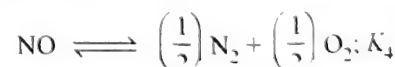
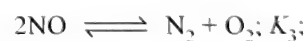
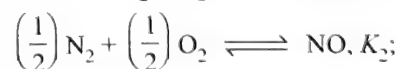
19. Which is/are correct?

- (1) $2.303 \log K = -\Delta H^\ominus/RT + \Delta S^\ominus/R$
- (2) $\Delta G^\ominus = -2.303RT \log K$
- (3) $-2.303 \log K = -\Delta H^\ominus/RT^2 + \Delta S^\ominus/R$
- (4) $2.303 \log K = (1/RT)(\Delta H^\ominus + \Delta S^\ominus)$

20. For the reaction, $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$, which is the the correct representation?

- (1) $K_p = (p_{CO_2})$
- (2) $K_p = K_c(RT)$
- (3) $K_p = (CO_2)/1$
- (4) None

21. $N_2 + O_2 \rightleftharpoons 2NO$, K_1 ;



Correct relation(s) between K_1 , K_2 , K_3 , and K_4 is/are

- (1) $K_1 \times K_3 = 1$
- (2) $\sqrt{K_1} \times K_4 = 1$
- (3) $\sqrt{K_3} \times K_2 = 1$
- (4) None

22. The rate of disappearance of A at two temperatures is given by $A \rightleftharpoons B$

i. $\frac{d[A]}{dt} = 2 \times 10^{-2} [A] - 4 \times 10^{-3} [B]$ at 300 K

ii. $\frac{d[A]}{dt} = 4 \times 10^{-2} [A] - 16 \times 10^{-4} [B]$ at 400 K

From the given values of heat of reaction which are incorrect.

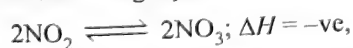
- (1) 3.86 kcal (2) 6.93 kcal
(3) 1.68 kcal (4) 1.68×10^{-2} kcal
23. Which of the following will favour the formation of NH_3 by Haber's process?
- (1) Increase in temperature
(2) Increase in pressure
(3) Addition of catalyst
(4) Addition of promoter
24. Which of the following will not affect the value of equilibrium constant of a reaction?
- (1) Change in the concentration of the reactants
(2) Change in temperature
(3) Change in pressure
(4) Addition of catalyst
25. Which of the following statements is/are wrong?
- (1) At equilibrium, concentrations of reactants and products become constant because the reaction stops.
(2) Addition of catalyst speeds up the forward reaction more than the backward reaction.
(3) Equilibrium constant of an exothermic reaction decreases with increase of temperature.
(4) K_p is always greater than K_c .
26. When NaNO_3 is heated in a closed vessel oxygen is liberated and NaNO_2 is left behind. At equilibrium, which are correct
- (1) Addition of NaNO_2 favours reverse reaction.
(2) Addition of NaNO_3 favours forward reaction.
(3) Increasing temperature favours forward reaction.
(4) Increasing pressure favours reverse reaction.

Linked Comprehension Type

Paragraph 1

Physical and chemical equilibrium can respond to a change in their pressure, temperature, and concentration of reactants and products. To describe the change in the equilibrium we have a principle named Le Chatelier's principle. According to this principle, even if we make some changes in equilibrium, then also the system even re-establishes the equilibrium by undoing the effect.

1. Consider the following equilibrium:



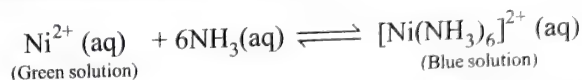
If O_2 is added and volume of the reaction vessel is reduced, the equilibrium

- (1) Shifts in the product side
(2) Shifts in the reactant side
(3) Cannot be predicted
(4) Remains unchanged
2. If we add SO_4^{2-} ion to a saturated solution of Ag_2SO_4 , it will result in a/an

- (1) Increase in Ag^+ concentration.
(2) Decrease in Ag^+ concentration.
(3) It will shift Ag^+ ions from solid Ag_2SO_4 into solution.
(4) It will decrease the SO_4^{2-} ion concentration in the solution.
3. In the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. If we increase the pressure of the system, the equilibrium is
- (1) Shifts in the product side (2) Shift in reactant side
(3) Remains unchanged (4) Cannot be predicted

Paragraph 2

Consider the chemical reaction:

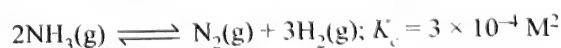
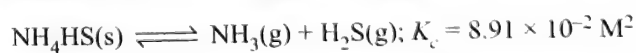


When $\text{H}^+(\text{aq})$ is added, the colour green is favoured. Use one or more of the following interpretations to answer the questions:

- i. Some unreacted $\text{Ni}^{2+}(\text{aq})$ is present in the solution at equilibrium
ii. Some unreacted $\text{NH}_3(\text{aq})$ is present in the solution at equilibrium
iii. The colour change indicates new equilibrium conditions with reduced $[\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq})$
iv. The colour change indicates new equilibrium conditions with increased $[\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq})$.
4. The deepening of blue colour on dissolving more $\text{Ni}(\text{NO}_3)_2$ supports interpretation(s).
- (1) i only (2) i and iv only
(3) ii and iv only (4) i and ii only
5. The deepening of blue colour on addition of more $\text{NH}_3(\text{aq})$ supports interpretation(s).
- (1) i only (2) i and iv only
(3) i and ii only (4) ii and iv only

Paragraph 3

One mole of $\text{NH}_4\text{HS}(\text{s})$ was allowed to decompose in a 1-L container at 200°C . It decomposes reversibly to $\text{NH}_3(\text{g})$ and $\text{H}_2\text{S}(\text{g})$. $\text{NH}_3(\text{g})$ further undergoes decomposition to form $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$. Finally, when equilibrium was set up, the ratio between the number of moles of $\text{NH}_3(\text{g})$ and $\text{H}_2(\text{g})$ was found to be 3.



Answer the following:

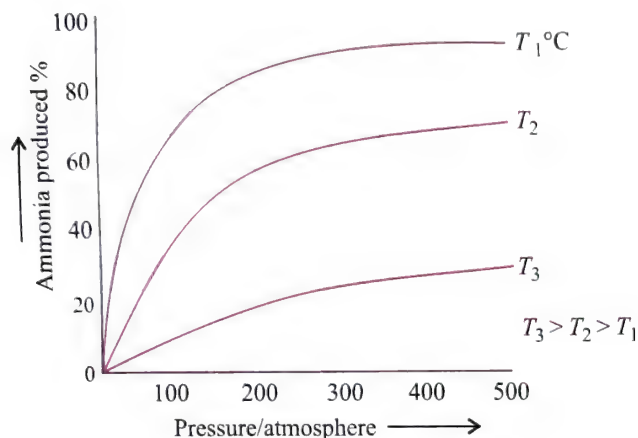
6. What is the mole fraction of hydrogen gas in the equilibrium mixture in the gas phase?
- (1) 1/4 (2) 3/4 (3) 1/8 (4) 4
7. To attain equilibrium, how much % by weight of solid NH_4HS got dissociated?
- (1) 19% (2) 30% (3) 33% (4) 15%

8. Assuming the volume due to solid NH_4HS is negligible what will be the density of the gaseous mixture in the above equilibrium system?

- (1) 16.83 g L^{-1} (2) 16.83 g mL^{-1}
(3) 18.415 g L^{-1} (4) 14.83 g L^{-1}

Paragraph 4

The percentage of ammonia produced from nitrogen and hydrogen under certain conditions of temperature and pressure is given in the graph

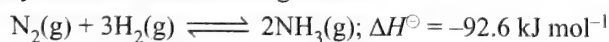


Use the graph answering the following questions:

9. What happens to the percentage of ammonia produced when the temperature is increased
- (1) The % is decreased (2) The % is increased
(3) No effect (4) Cannot be predicted
10. What happens to the percentage of ammonia produced when the pressure is increased?
- (1) The % is increased (2) The % is decreased
(3) No effect (4) Cannot be predicted
11. What conditions of pressure produce the highest percentage of ammonia?
- (1) At least 50 atm (2) At least 150 atm
(3) At least 300 atm (4) At least 100 atm

Paragraph 5

The synthesis of ammonia is given as:



given $K_c = 1.2$ and temperature $(T) = 375^\circ\text{C}$.

Answer the followings:

12. The expression of equilibrium constant is

- (1) $K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$ (2) $K_c = \frac{[\text{N}_2][\text{H}_2]}{[\text{NH}_3]}$
(3) $K_c = \frac{[\text{NH}_3]}{[\text{N}_2][\text{H}_2]^3}$ (4) $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

13. On increasing the temperature, the value of equilibrium constant K_c

- (1) Increases (2) Decreases
(3) Remain unchanged (4) Cannot be predicted

14. The relationship between K_p and K_c for this reaction is

- (1) $K_c = K_p(RT)^2$ (2) $K_p = K_c(RT)^{-1}$
(3) $K_p = K_c(RT)^2$ (4) $K_p = K_c(RT)^4$

15. Which of the following factors does not increase the yield of NH_3 at equilibrium?

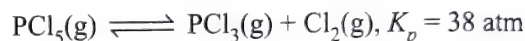
- (1) Catalyst (2) Increase in pressure
(3) Increase in temperature (4) Decrease in pressure

16. Starting with 2 mol of each (N_2 , H_2 and NH_3) in 5.0 L reaction vessel at 375°C , predict what is true for the reaction?

- (1) The reaction is at equilibrium
(2) The reaction proceed in forward direction.
(3) The reaction proceed in backward direction.
(4) Q_c for the reaction is less then K_c .

Paragraph 6

Phosphorous pentachloride when heated in a sealed tube at 700 K undergoes decomposition as



Vapour density of the mixture is 74.25.

Answer the following questions:

17. The reaction is

- (1) Endothermic
(2) Exothermic
(3) May be endothermic or exothermic
(4) Unpredictable

18. Percentage dissociation of PCl_5 may be given as

- (1) 4.04 (2) 40.4 (3) 44.0 (4) 0.404

19. Equilibrium constant K_c for the reaction will be

- (1) 0.66 M (2) 0.56 M (3) 0.46 M (4) 0.36 M

20. If pressure is increased then the equilibrium will

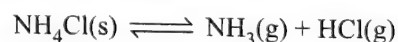
- (1) Be unaffected
(2) Shift in backward direction
(3) Shift in forward direction
(4) Cannot be predicted

21. When an inert gas is added to the given reversible process, then the equilibrium will.

- (1) Be unaffected
(2) Shift in backward direction
(3) Shift in forward direction
(4) Cannot be predicted

Paragraph 7

Decomposition of ammonium chloride is an endothermic reaction. The equilibrium may be represented as:



A 6.250 g sample of NH_4Cl is placed in an evacuated 4.0 L container at 27°C . After equilibrium the total pressure inside the

container is 0.820 bar and some solid remains in the container.
Answer the followings

22. The value of K_p for the reaction at 300 K is
(1) 16.2 (2) 0.168 (3) 1.68 (4) 32.4
23. The amount of solid NH_4Cl left behind in the container at equilibrium is
(1) 2.856 (2) 28.56 (3) 0.2856 (4) 1.320
24. If the volume of container were doubled at constant temperature, then what would happen to the amount of solid in the container.
(1) Decrease (2) Increases
(3) Remain unchanged (4) None
25. The extent of decomposition can be increased by
(1) Increasing the temperature
(2) Decreasing the temperature
(3) Adding more NH_4Cl
(4) Removing HCl(g)
26. The value of K_p for the reaction decreases with
(1) Increase in volume (2) Decrease in temperature
(3) Decrease in pressure (4) Increase in temperature

Paragraph 8

K_p and K_c are inter related as

$$K_p = K_c(RT)^{\Delta n}$$

Answer the following questions:

27. Which of the following have $K_p = K_c$?
(1) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
(2) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
(3) $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$
(4) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
28. Which of the following have same units of K_p ?
(1) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
(2) $\text{AB}_2(\text{g}) \rightleftharpoons \text{AB}(\text{g}) + \text{B}(\text{g})$
(3) $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
(4) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
29. In which of the following equilibria K_p is less than K_c ?
(1) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
(2) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
(3) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$
(4) $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
30. For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$; K_p/K_c is equal to:
(1) RT^3 (2) $1/RT$ (3) $(RT)^4$ (4) $1/(RT)^2$
31. The unit of equilibrium constant for
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

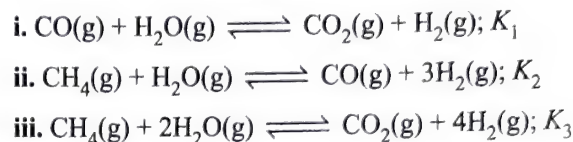
- (1) mol L^{-2} (2) $\text{mol}^2 \text{L}^{-2}$
(3) L mol^{-2} (4) None of these

Paragraph 9

The relation between K_p and K_c is $K_p = K_c(RT)^{\Delta n}$ unit of $K_p = (\text{atm})^{\Delta n}$; unit of $K_c = (\text{mol L}^{-1})^{\Delta n}$.

Answer the following:

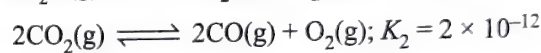
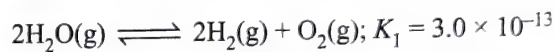
32. Consider the following reactions:



Which of the following is correct?

- (1) $K_3 = K_1/K_2$ (2) $K_3 = K_1^2/K_2^3$
(3) $K_3 = K_1 \times K_2$ (4) $K_3 = K_1\sqrt{K_2}$

33. The equilibrium constants of the following reactions at 400 K are given:



Then, the the equilibrium constant K for the reaction



is

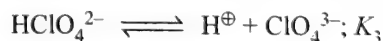
- (1) 2.04 (2) 20.5 (3) 0.85 (4) 1.4

34. Given: $2\text{NO(g)} + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); K_1$
 $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}); K_2$
 $2\text{NO(g)} + \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}); K_3$

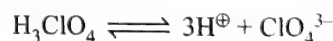
Which of the following relations is correct?

- (1) $K_3 = K_1/K_2$ (2) $K_3 = K_1 \times K_2$
(3) $K_3 = K_1 + K_2$ (4) $K_3 = K_1/\sqrt{K_2}$

35. H_3ClO_4 is a tribasic acid, it undergoes ionisation as

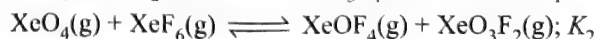
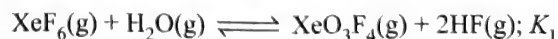


Then, equilibrium constant for the following reaction will be:

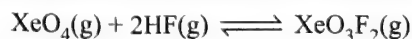


- (1) $K_1K_2K_3$ (2) $\frac{(K_1K_3)^2}{K_2}$ (3) $\frac{K_1}{K_2}$ (4) $\frac{K_1K_2}{K_3^2}$

36. Consider the two reactions:

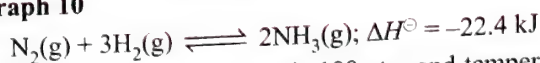


Then, the equilibrium constant for the following reaction



is given by:

- (1) K_1/K_2^2 (2) $(K_1/K_2)^{1/2}$ (3) K_1^2/K_2^3 (4) K_2/K_1

Paragraph 10

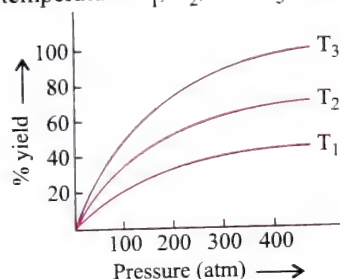
The pressure inside the chamber is 100 atm and temperature at 300 K.

Answer the following questions:

37. If K_p for the given reaction is 1.44×10^{-5} , then the value of K_c will be:

(1) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}} \text{ mol L}^{-1}$ (2) $\frac{1.44 \times 10^{-5}}{(8.314 \times 200)^{-2}} \text{ mol L}^{-1}$
 (3) $\frac{1.44 \times 10^{-5}}{(0.082 \times 700)^{-2}} \text{ mol L}^{-1}$ (4) $\frac{1.44 \times 10^{-5}}{(0.082 \times 300)^{-2}} \text{ mol L}^{-1}$

38. The preparation of ammonia by Haber's process is an exothermic reaction. If the preparation follows the following temperature-pressure relationship for its % yield. Then for temperature T_1 , T_2 , and T_3 the correct option is:

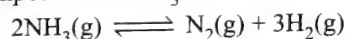


- (1) $T_3 > T_2 > T_1$ (2) $T_1 > T_2 > T_3$
 (3) $T_3 < T_2 < T_1$ (4) $T_1 = T_2 = T_3$

39. On adding catalyst the equilibrium of reaction:

- (1) Shift in backward direction
 (2) Shift in forward direction
 (3) Does not affect the equilibrium
 (4) Cannot predict.

40. If K_p for the reaction is 1.44×10^{-5} , then the value of K_p for the decomposition of NH_3



will be:

- (1) $\sqrt{1.44 \times 10^{-5}}$ (2) $(1.44 \times 10^{-5})^4$
 (3) $\frac{1}{1.44 \times 10^{-5}}$ (4) 1.00×10^{-3}

41. 30 L $\text{H}_2(\text{g})$ and 30 L $\text{N}_2(\text{g})$ were taken for the reaction in Haber's process which yields only 50% of the expected ammonia due to reversibility of the reaction. What will be the composition of reaction mixture under the given condition?

NH_3	N_2	H_2
(1) 20 L	20 L	20 L
(2) 10 L	25 L	15 L
(3) 20 L	10 L	30 L
(4) 20 L	25 L	15 L

Paragraph 11

Mass action ratio or reaction quotient Q for a reaction can be calculated using the law of mass action



$$Q = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

The value of Q decides whether the reaction is at equilibrium or not.

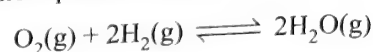
At equilibrium, $Q = K$

For an equilibrium process, $Q \neq K$

when $Q > K$, reaction will favour backward direction and when $Q < K$, it will favour forward direction.

Answer the following questions:

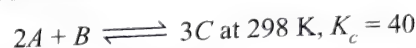
42. The reaction quotient Q for:



is given by $Q = \frac{[\text{H}_2\text{O}]^2}{[\text{O}_2][\text{H}_2]^2}$. The reaction will proceed in backward direction, when

- (1) $Q = K_c$ (2) $Q < K_c$ (3) $Q > K_c$ (4) $Q = 0$

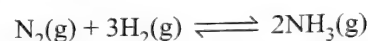
43. For the reaction:



A 4 L vessel contains 2, 1, and 4 mol of A, B, and C, respectively. The reaction at the same temperature

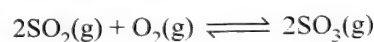
- (1) Must proceed in forward direction
 (2) Must proceed in backward direction
 (3) Must be in equilibrium
 (4) Cannot be predicted

44. In a reaction mixture containing H_2 , N_2 and NH_3 at partial pressure of 2 atm, 1 atm and 3 atm respectively, the value of K_p at 700 K is $4.00 \times 10^{-5} \text{ atm}^{-2}$. In which direction the net reaction will go?



- (1) Forward (2) Backward
 (3) No reaction (4) Cannot be predicted

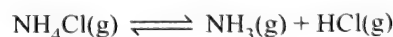
45. In the following reaction:



the equilibrium is not attained. The rate of forward reaction is greater than that of backward reaction. Thus, which of the following is the correct relation between K_p and Q_p ?

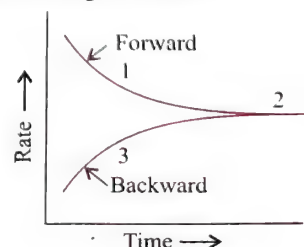
- (1) $K_p = Q_p$ (2) $Q_p > K_p$
 (3) $Q_p < K_p$ (4) $K_p = Q_p = 1$

46. In the reaction:



a graph is plotted to show that the variation or the rate of forward and backward reactions against time.

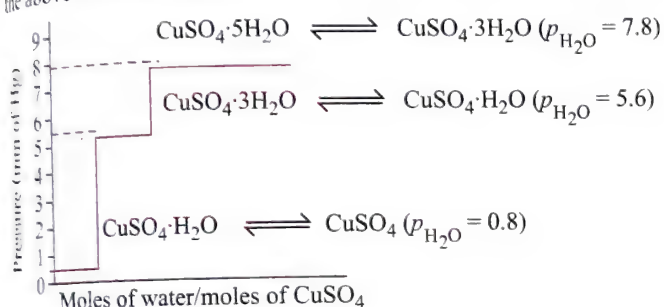
Which of following is correct?



	$Q > K$	$Q = K$	$Q < K$
(1)	3	2	1
(2)	2	3	1
(3)	1	2	3
(4)	2	1	3

Paragraph 12

Dehydration of salts is an important class of heterogeneous reactions. The salt hydrates during dehydration often dissociate in steps to form a number of intermediate hydrates according to the prevailing pressure of moisture in contact with the solid hydrates. Thus, copper sulphate pentahydrate on dissociation yields trihydrates, monohydrates and then the anhydrous salt in the above order as follows:



47. The equilibrium constant K_p for the equilibrium between pentahydrate and trihydrate is:

- (1) 7.8 (2) 60.84 (3) 31.36 (4) 5.6

48. The ratio of equilibrium constant between pentahydrate and trihydrate and equilibrium between trihydrate and monohydrate is

- (1) 1.9 (2) 2.9 (3) 8.6 (4) 5.6

49. Which of the following conditions is favourable for dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?

- i. Low humidity in air ii. High temperature
iii. $p_{\text{H}_2\text{O}}$ increases

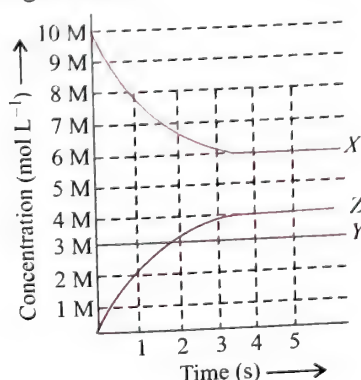
The correct option is:

- (1) i (2) i, ii (3) ii, iii (4) i, ii, iii

Paragraph 13

X, Y and Z react in the 1:1:1 stoichiometric ratio.

The concentration of X, Y and Z we are found to vary with time as shown in the figure below:



50. Which of the following equilibrium reaction represents the correct variation of concentration with time?

- (1) $X(g) + Y(g) \rightleftharpoons Z(g)$
 (2) $X(g) + Y(s) \rightleftharpoons Z(g)$
 (3) $Z(g) + Y(g) \rightleftharpoons X(g)$
 (4) $Z(g) + X(g) \rightleftharpoons Y(g)$

51. The value of the equilibrium constant (K_c) for the equilibrium represented the in above sketch will be

- (1) $\frac{9}{2}$ (2) $\frac{11}{4}$
 (3) $\frac{2}{3}$ (4) $\frac{10}{7}$

52. If the above equilibrium is established in a 2.0 L container by taking reactants in sufficient amount then how many moles of component Y must have reacted to establish the equilibrium?

- (1) 0 (2) 6 (3) 12 (4) 8

Paragraph 14

Two solids X and Y dissociate into gaseous products at a certain temperature as follows:

i. $X(s) \rightleftharpoons A(g) + C(g)$ and

ii. $Y(s) \rightleftharpoons B(g) + C(g)$

At a given temperature, pressure over excess solid 'X' is 40 mm of Hg and total pressure over solid 'Y(s)' is 60 mm of Hg.

Now, answer the following questions:

53. Ratio of K_p for reaction (i) to that of reaction (ii), is:

- (1) 4:9 (2) 2:3 (3) 4:9 (4) 2:1

54. The ratio of moles of A and B in the vapour state over a mixture of solids X and Y, is:

- (1) 2:3 (2) 2:5 (3) 4:9 (4) 1:1

55. The total pressure of gasses over a mixture of solids X and Y is:

- (1) 100 mm (2) 74.84 mm
 (3) 50 mm (4) 120.74 mm

Matrix Match Type

This section questions each with two columns I and II. Match the items given in column I with that of column II.

1.

	Column I	Column II
a.	$Q = K$	p. Reaction is nearer to completion
b.	$Q < K$	q. Reaction is not at equilibrium
c.	$Q < K$	r. Reaction is fast in forward direction
d.	$K \gg 1$	s. Reaction at equilibrium
		t. Reaction proceeds in backward direction

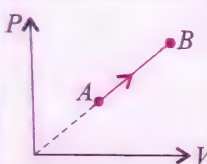
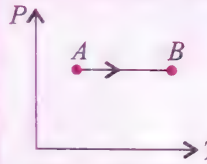
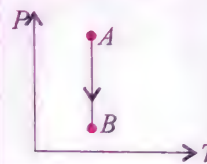
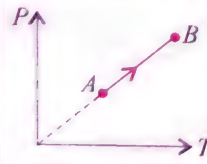
2.

Column I	Column II
a. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2$	p. $K_p = K_c$
b. $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	q. K increase with increase in temperature
c. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	r. On increasing pressure reaction favour to product side
	s. $K_c > K_p$

3.

Column I	Column II
a. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	p. mol L^{-1}
b. $\text{NH}_4\text{Cl}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$	q. Unitless
c. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	r. atm
d. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	s. atm^{-2}

4.

Column I	Column II
a. 	p. Temperature is increasing
b. 	q. Temperature is constant
c. 	r. Volume is constant
d. 	s. Pressure is increasing

5.

Column I	Column II
a. Dissociation of $\text{N}_2\text{O}_4(\text{g})$ $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g});$ $\Delta H = +57.0 \text{ kJ}$	p. Increases with temperature

b. Oxidation of $\text{NH}_3(\text{g})$ $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ $\Delta H = -900.0 \text{ kJ}$	q. Decreases with pressure
c. Oxidation of nitrogen $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g});$ $\Delta H = +180.0 \text{ kJ}$	r. Increases with addition of inert gas at constant pressure
d. Formation of $\text{NO}_2(\text{g})$ $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g});$ $\Delta H = -200 \text{ kJ}$	s. Decreases with temperature

6.

Column I	Column II
a. Reaction is reversed	p. $(K)^{1/2}$
b. Reaction is divided by 2	q. K^2
c. Reaction is multiplied by 2	s. $1/K$

7.

Column I	Column II
a. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	p. Forward shift by rise in pressure
b. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g});$ $\Delta H = -\text{ve}$	q. Unaffected by change in pressure
c. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g});$ $\Delta H = +\text{ve}$	r. Forward shift by rise in temperature
d. $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g});$ $\Delta H = +\text{ve}$	s. Forward shift by lowering the temperature

8.

Column I	Column II
a. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	p. $K_p = K_c(RT)$
b. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	q. $K_p = K_c(RT)^{-2}$
c. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	r. $K_p = K_c(RT)^{-2}$
d. $\text{NH}_4\text{Cl}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$	s. $K_p = K_c$

9.

Column I	Column II
a. Addition of inert gas at constant pressure shifts the equilibrium in backward direction	p. $\Delta V \neq 0, \Delta n > 0$
b. Addition of inert gas at constant pressure has no effect on equilibrium	q. $\Delta V \neq 0, \Delta n < 0$

c. $K_p = K_c$	r. $\Delta V = 0$
d. Addition of inert gas shift the equilibrium in forward direction at constant P	s. $\Delta n = 0$

10.

Column I	Column II
a. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	p. Unaffected by inert gas addition
b. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	q. Forward shift by rise in pressure and backward shift by inert gas addition
c. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	r. Unaffected by increase in pressure
d. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	s. Backward shift by rise in pressure and forward shift by inert gas addition

11.

Column I	Column II
a. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	p. Effect of concentration pressure and temperature on a system at equilibrium
b. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	q. Irreversible reaction
c. Le Chatelier's principle	r. Law of mass action
d. $K_p = K_c$	s. Equilibrium state
e. $2\text{Mg} + \text{O}_2 \longrightarrow 2\text{MgO}$	t. Homogeneous reversible reaction
f. Rate of forward reaction = Rate of backward reaction	u. Heterogeneous reversible reaction
g. Guldberg and Waage	v. $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

Numerical Value Type

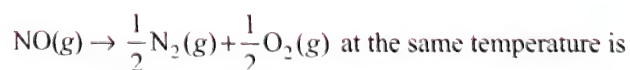
- A reaction attains equilibrium, when the free energy change is
(1) 1 (2) 2
(3) 3 (4) 0
- For a homogeneous chemical reaction, $K_p = K_c$ when
(1) $\Delta n = 0$ (2) $\Delta n = 1$
(3) $\Delta n = 2$ (4) $\Delta n = \infty$
- For the reaction $A + B \rightleftharpoons C$, the rate constants for the forward and the reverse reactions are 4×10^2 and 2×10^2 respectively. The value of equilibrium constant K for the reaction would be
(1) 1 (2) 2
(3) 3 (4) 4
- The equilibrium constant for the reactions $A + B \rightleftharpoons AB$ is 0.5 at 200 K. The equilibrium constant for the reaction $AB \rightleftharpoons A + B$ would be
(1) 1 (2) 2
(3) 3 (4) 4
- One mole of ethanol is treated with one mole of ethanoic acid at 25°C . Half of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be
(1) 1 (2) 2
(3) 3 (4) 4
- In the reaction $A + B \rightleftharpoons AB$, if the concentration of A and B is increased by a factor of 2, it will cause the equilibrium concentration of AB to change to
(1) Two times to original value
(2) Three times to original value
(3) Same
(4) Zero
- At equilibrium, the value of equilibrium constant K is
(1) 1 (2) 2
(3) 3 (4) 0

Archives

JEE MAIN

Single Correct Answer Type

- A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is
(1) 1.8 atm (2) 3 atm
(3) 0.3 atm (4) 0.18 atm
(AIEEE 2011)
- The equilibrium constant (K_c) for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$ at temperature T is 4×10^{-4} . The value of K_c for the reaction



- (1) 0.02 (2) 2.5×10^2
(3) 4×10^{-4} (4) 50 (AIEEE 2012)
- For the reaction,
$$\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}),$$

If $K_p = K_c (RT)^x$ where the symbols have usual meanings, then, the value of x is (assuming ideality).
(1) -1 (2) -1/2 (3) 1/2 (4) 1
(JEE Main 2014)

4. The standard Gibbs energy change at 300 K for the reaction $2A \rightarrow B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the

$$[R = 8.314 \text{ J/K/mol}, e = 2.718]$$

- (1) forward direction because $Q > K_C$
- (2) reverse direction because $Q > K_C$
- (3) forward direction because $Q < K_C$
- (4) reverse direction because $Q < K_C$

(JEE Main 2015)

5. The equilibrium constants at 298 K for a reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be:

- (1) 1.182
- (2) 0.182
- (3) 0.818
- (4) 1.818

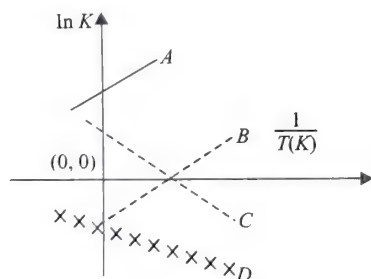
(JEE Main 2016)

6. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl . If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is:

- (1) 3×10^{-20}
- (2) 6×10^{-21}
- (3) 5×10^{-19}
- (4) 5×10^{-8}

(JEE Main 2018)

7. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction?



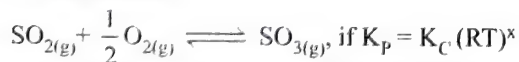
- (1) B and C
- (2) C and D
- (3) A and D
- (4) A and B

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. For the reaction,



where the symbols have usual meaning then the value of x is: (assuming ideality)

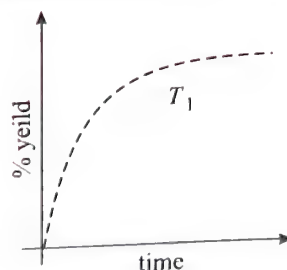
- (1) $\frac{1}{2}$
- (2) 1
- (3) -1
- (4) $-\frac{1}{2}$

(JEE Advanced 2014)

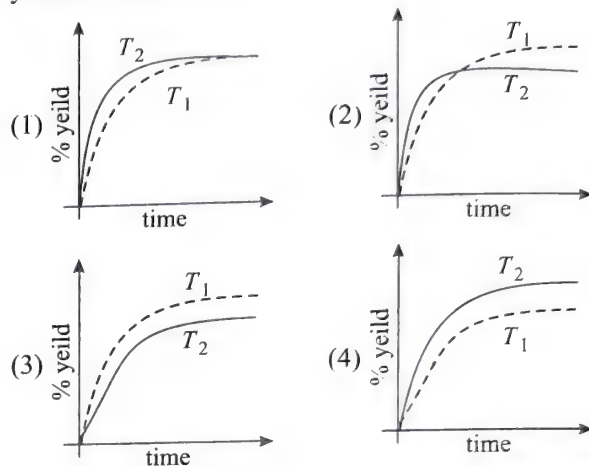
2. The % yield of ammonia as a function of time in the reaction



at (P, T_1) is given below.

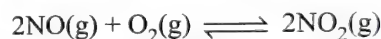


If this reaction is conducted at (P, T_2) , with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by



(JEE Advanced 2015)

3. The following reaction is performed at 298 K.



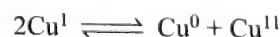
The standard free energy of formation of $\text{NO}(g)$ is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $\text{NO}_2(g)$ at 298 K? ($K_p = 1.6 \times 10^{12}$)

- (1) $R(298) \ln(1.6 \times 10^{12}) - 86600$
- (2) $86600 + R(298) \ln(1.6 \times 10^{12})$
- (3) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$
- (4) $0.5[2 \times 86600 - R(298) \ln(1.6 \times 10^{12})]$

(JEE Advanced 2015)

Multiple Correct Answers Type

1. The equilibrium

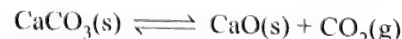


in aqueous medium at 25°C shifts towards the left in the presence of

- (1) NO_3^-
- (2) Cl^-
- (3) SCN^-
- (4) CN^-

(IIT-JEE 2011)

2. The thermal dissociation equilibrium of $\text{CaCO}_3(s)$ is studied under different conditions.



For this equilibrium, the correct statement(s) is(are)

- (1) ΔH is dependent on T
- (2) K is independent of the initial amount of CaCO_3

(3) K is dependent on the pressure of CO_2 at a given T

(4) ΔH is independent of the catalyst, if any

(JEE Advanced 2013)

3. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

(1) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

(2) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

(3) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases

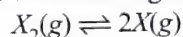
(4) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system negative

(JEE Advanced 2017)

Linked Comprehension Type

Paragraph 1

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:



The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X . As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given: $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

(JEE Advanced 2016)

1. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is

(1) $\frac{8\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$ (2) $\frac{8\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

(3) $\frac{4\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$ (4) $\frac{4\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

2. The INCORRECT statement among the following, for this reaction, is

(1) Decrease in the total pressure will result in formation of more moles of gaseous X

(2) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(3) $\beta_{\text{equilibrium}} = 0.7$

(4) $K_C < 1$

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|---------|------------|-----------|---------|---------|
| 1. (4) | 2. (4) | 3. (2) | 4. (3) | 5. (2) |
| 6. (3) | 7. (1) | 8. (3) | 9. (3) | 10. (2) |
| 11. (3) | 12. (2) | 13. (2) | 14. (4) | 15. (2) |
| 16. (3) | 17. (3) | 18. (2) | 19. (4) | 20. (4) |
| 21. (2) | 22. (2) | 23. (2) | 24. (3) | 25. (3) |
| 26. (4) | 27. (3) | 28. (4) | 29. (3) | 30. (1) |
| 31. (1) | 32. (4) | 33. (3) | 34. (4) | 35. (3) |
| 36. (1) | 37. (2) | 38. (2) | 39. (1) | 40. (2) |
| 41. (4) | 42. (2) | 43. (1) | 44. (4) | 45. (1) |
| 46. (3) | 47. (4) | 48. (2,4) | 49. (1) | 50. (3) |
| 51. (1) | 52. (2, 4) | 53. (4) | 54. (1) | 55. (4) |
| 56. (4) | | | | |

Multiple Correct Answers Type

- | | | |
|-----------------|-----------------|--------------|
| 1. (2, 3) | 2. (1, 3) | 3. (1, 2, 4) |
| 4. (1, 2, 3, 4) | 5. (1, 2, 3, 4) | 6. (2, 4) |
| 7. (1, 2, 3, 4) | 8. (2, 3, 4) | 9. (2, 3, 4) |

10. (1, 2, 4)

13. (1)

16. (1, 3, 4)

19. (1, 2)

22. (2, 3, 4)

25. (1, 2, 4)

11. (2, 3, 4)

14. (1, 3, 4)

17. (1, 2)

20. (1, 2, 3)

23. (2, 3, 4)

26. (3, 4)

12. (2, 3, 4)

15. (2, 3, 4)

18. (2, 3)

21. (1, 2, 3)

24. (1, 2, 4)

Linked Comprehension Type

- | | | | | |
|---------|------------|------------|---------|---------|
| 1. (1) | 2. (2) | 3. (1) | 4. (2) | 5. (4) |
| 6. (2) | 7. (3) | 8. (1) | 9. (1) | 10. (3) |
| 11. (3) | 12. (2) | 13. (2) | 14. (1) | 15. (1) |
| 16. (3) | 17. (1) | 18. (2) | 19. (1) | 20. (2) |
| 21. (3) | 22. (2) | 23. (1) | 24. (1) | 25. (1) |
| 26. (2) | 27. (1, 2) | 28. (1, 2) | 29. (2) | 30. (4) |
| 31. (4) | 32. (3) | 33. (4) | 34. (2) | 35. (1) |
| 36. (4) | 37. (4) | 38. (2) | 39. (3) | 40. (3) |
| 41. (2) | 42. (3) | 43. (1) | 44. (2) | 45. (3) |
| 46. (1) | 47. (2) | 48. (1) | 49. (2) | 50. (3) |
| 51. (3) | 52. (4) | 53. (1) | 54. (3) | 55. (2) |

Matrix Match Type

Q.No.	a.	b.	c.	d.	e.	f.	g.
1.	s	q, r	q, t	p	—	—	—
2.	q	p	r, s	—	—	—	—
3.	p, r	p, r	q	s	—	—	—
4.	p, s	p, r, s	q, r	p, s	—	—	—
5.	p, r	q, r, s	p	s	—	—	—
6.	r	p	p	—	—	—	—
7.	p, s	p, s	q, r	p, r	—	—	—
8.	s	r	p	q	—	—	—
9.	p	r	s	q	—	—	—
10.	p, r	p, r	q	s	—	—	—
11.	t	u	p	v	q	s	r

Numerical Value Type

1. (4) 2. (1) 3. (2) 4. (2) 5. (1)
6. (1) 7. (1)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (1) 2. (4) 3. (2) 4. (2) 5. (4)
6. (1) 7. (1)

JEE Advanced**Single Correct Answer Type**

1. (4) 2. (3) 3. (4)

Multiple Correct Answers Type

1. (2, 3, 4) 2. (1, 2, 4) 3. (2, 3)

Linked Comprehension Type

1. (2) 2. (3)

OVERVIEW

1. Strong and Weak Electrolytes

Electrolyte which dissociates almost completely into ions in aqueous solution is called **strong electrolyte** (e.g., H_2SO_4 , NaCl , HCl etc.) whereas an electrolyte which dissociates to a lesser extent in aqueous solution is called a weak electrolyte (e.g., CH_3COOH , NH_4OH etc.) The fraction of the total number of molecules which dissociates into ions is called degree of dissociation (or ionization) and is represented as α .

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Total number of molecules}}$$

The degree of dissociation depends on the following factors:

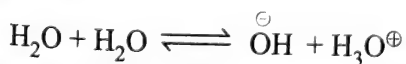
- Nature of the solute:** All ionic compounds i.e., strong electrolytes have $\alpha \approx 1$ at normal dilution. Most of the polar covalent compounds i.e., weak electrolytes have $\alpha < 1$.
- Nature of the solvent:** Polar solvents with high dielectric constant are more ionizing.
- Concentration:** Degree of ionization is inversely proportional to concentration.
- Temperature:** Degree of ionization is directly proportional to temperature.
- Addition of other species:** Addition of another solute having an ion common to that of weak electrolyte results in the suppression of the degree of dissociation of weak electrolyte (common ion effect).

2. Acid and base

a. **Arrhenius concept:** Acid is proton donor and base is hydroxyl ion donor.

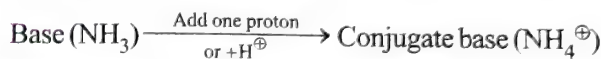
b. **Bronsted concept**

- An acid is a proton donor, a base is a proton acceptor.
- The strength of an acid depends upon its tendency to donate proton. More is the tendency to donate proton, more is the acidic nature.
- Water is amphoteric as it donates as well as accepts proton.



iv. Each cation is acid and each anion is base.

v. A pair of acid and base which differ by a proton is known as conjugate pair of acid and base.



c. Lewis concept

- Acids are electron pair acceptor, e.g., BF_3 , AlCl_3 .
- Bases are electron pair donor, e.g., NH_3 , PCl_3 .

3. Relative strength of acids and bases

a. For weak acids:

$$\begin{aligned} \text{Relative strength} &= \frac{\text{Strength of I acid}}{\text{Strength of II acid}} \\ &= \frac{[\text{H}^+] \text{ furnished by I acid}}{[\text{H}^+] \text{ furnish by II acid}} = \frac{C_1 \alpha_1}{C_2 \alpha_2} \\ &= \frac{C_1}{C_2} \times \sqrt{\frac{K_{a1} C_2}{K_{a2} C_1}} = \sqrt{\frac{K_{a1} C_1}{K_{a2} C_2}} \\ &= \sqrt{\frac{K_{a1}}{K_{a2}}} \quad (\text{if } C_1 = C_2) \end{aligned}$$

Similarly,

$$\frac{\text{Strength of the base (BOH)}_1}{\text{Strength the base (BOH)}_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

When pH of two acids are same:

$$[\text{H}^+]_1 = [\text{H}^+]_2$$

$$C_1 \alpha_1 = C_2 \alpha_2$$

$$\frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$\frac{K_{a1}}{K_{a2}} = \frac{C_2}{C_1}$$

b. For strong acids:

Relative strength

$$= \frac{K_1}{K_2}$$

$$= \frac{\text{Rate constant for a reaction catalysed by acid I}}{\text{Rate constant for a reaction catalysed by acid II}}$$

Note: Hydrolysis of ester in acidic medium follows first-order kinetics whereas hydrolysis of ester in basic medium (i.e., saponification of ester) follows second-order kinetics.

- Arrhenius theory is valid only for aqueous solutions.
- In complex compounds, the metal atoms (or ions) act as Lewis acids while the ligands act as Lewis base.
- Acids like HCl, HBr, HI, HNO₃ and H₂SO₄ are strong acids whereas H₂CO₃, H₂S, HCN and CH₃COOH etc., are weak acids.
- The increasing order of acidic strength of some acids is
 $\text{CH}_4 < \text{H}_2\text{O} < \text{H}_2\text{CO}_3 < \text{NH}_4^+ < \text{H}_2\text{S} < \text{CH}_3\text{COOH} < \text{HF} < \text{HSO}_4^- < \text{H}_3\text{O}^+ < \text{HCl} < \text{H}_2\text{SO}_4 < \text{HBr} < \text{HI} < \text{HClO}_4$
- The increasing order of basic strength of some bases is
 $\text{ClO}_4^- < \text{HSO}_4^- < \text{Cl}^- < \text{H}_2\text{O} < \text{SO}_4^{2-} < \text{F}^- < \text{CH}_3\text{COO}^- < \text{HS}^- < \text{NH}_3 < \text{CO}_3^{2-} < \text{OH}^- < \text{S}^{2-} < \text{O}^{2-} < \text{CH}_3^-$
- The strength of acid depends upon the nature of solvent. For example, HCl, HNO₃, H₂SO₄ and HClO₄ have same strength in water. It is due to levelling effect of water. In acetic acid solvent, the strength of above acids follow the order
 $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$
 Thus, acetic acid is called as differentiating solvent since acetic acid behaves as such a weak base that it will accept protons from the stronger acid more readily than from the weaker acid.
- Levelling effect of water is due to its high dielectric constant and strong proton accepting tendency.
- HClO₄ is the strongest while HCN is the weakest hydracid acid known. CsOH is the strongest base known.
- Acetic acid behaves as a strong acid in ammonia and as a base in anhydrous HF.
- Some periodic trends for acidity are:
 - In any group as we go down, the strength of hydracids increases due to increase in the size of the atom or anion.
 e.g. HF < HCl < HBr < HI and
 $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$
 - Among oxyacids of the same element, acidic nature increases with increase in its oxidation number
 e.g., $\text{HClO}^{(+1)} < \text{HClO}_2^{(+3)} < \text{HClO}_3^{(+5)} < \text{HClO}_4^{(+7)}$
 - Among oxyacids of the same type formed by different elements, acidic nature increase with electronegativity
 $\text{HIO}^{(2.4)} < \text{HBrO}_4^{(2.8)} < \text{HClO}_4^{(3.0)}$
 - Acidic nature of the hydride increases with increase in the electronegativity of the central atom.
 $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$
 - Among hydrides of element with same electronegativity acidic nature increases with the size of the central atoms
 $\text{CH}_4 < \text{H}_2\text{S} < \text{HI}$

14. Types of Solvents

On the basis of proton interaction, solvents can be classified into four types:

- Protophilic solvents are the solvents which have the tendency to accept protons e.g., H₂O, C₂H₅OH, liquid NH₃ etc.
 - Protogenic solvents are those which have the tendency to give protons e.g., water, liquid HCl, glacial CH₃COOH etc.
 - Amphiprotic solvents are those which act both as protophilic or protogenic solvents e.g., H₂O, NH₃, C₂H₅OH etc.
 - Aprotic solvents are those which neither donate nor accept protons e.g., benzene, CCl₄ etc.
15. Species classified as Bronsted acids are also acids according to Arrhenius concept. But all the species classified as bases according to Bronsted concept may not be Arrhenius bases. Some examples of such species are OCl⁻, H₂PO₄⁻, HCO₃⁻ etc.
16. A conjugate pair of acid and a base differs by a proton only i.e.
- $$\text{Conjugate acid} \rightleftharpoons \text{Conjugate base} + \text{H}^+$$
17. A strong Bronsted acid has a weak conjugate base and vice versa.
18. Each conjugate acid has one extra proton while each conjugate base has one proton less.
19. All Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.
20. **Ostwald's dilution law**
 It deals with the effect of dilution on weak electrolytes (weak acid or weak base). Degree of dissociation of weak electrolytes is proportional to the square root of dilution.
- $$K_a = \frac{C\alpha^2}{1 - \alpha^2}$$
- where K_a = dissociation constant of weak electrolyte
 α = degree of dissociation
 C = initial concentration of weak electrolyte
- If $\alpha \ll 1$, then $\alpha = \sqrt{\frac{K}{C}}$
- $$[\text{H}_3\text{O}^+] = C\alpha = \sqrt{K_a C}$$
- a. In case of weak monobasic acid:**
- $$K_a = \frac{[\text{H}^+]}{C - [\text{H}^+]} = \frac{C\alpha^2}{1 - \alpha}; \quad C = [\text{H}^+] + \frac{[\text{H}^+]}{K_a}$$
- If $1 - \alpha \approx 1$, then $K_a = C\alpha^2$ and $[\text{H}^+] = \sqrt{K_a C}$
- $$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (K_a C)^{1/2}$$
- $$\text{pH} = \frac{1}{2}(\text{p}K_a - \log C)$$
- b. In case of weak monoacidic base:**
- $$K_b = \frac{[\text{OH}^-]}{C - [\text{OH}^-]} = \frac{C\alpha^2}{1 - \alpha}; \quad C = [\text{OH}^-] + \frac{[\text{OH}^-]}{K_b} \quad \dots(\text{ii})$$
- If $1 - \alpha \approx 1$, then $K_b = C\alpha^2$ and $[\text{OH}^-] = \sqrt{K_b C} \quad \dots(\text{i})$

$$pOH = \frac{1}{2}[pK_b - \log C]$$

$$\text{or } pH = 14 - pOH = 14 - \frac{1}{2}[pK_b - \log C]$$

Equations (i) and (ii) are applied only when $\alpha \ll 1$ and the value of C must be high.

c. **Total $[OH^-]$ in mixture of two weak acids:**

$$[H_3O^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

d. **Total $[H_3O^+]$ in a mixture of two weak bases:**

$$[OH^-] = \sqrt{K_{b1}C_1 + K_{b2}C_2}$$

e. **Total $[H_3O^+]$ in a mixture of weak acid and a strong acid:**

$$[H_3O^+] = \frac{C_2 + \sqrt{C_2^2 + 4K_1C_1}}{2}$$

Here, C_1 is the concentration of weak acid having dissociation constant K_1 and C_2 is the concentration of strong acid.

i. For any acid-conjugate base pair, $K_a \cdot K_b = K_w$

$$\text{or } pK_w = pK_a + pK_b$$

ii. ' α ' of a weak electrolyte increases on dilution.

Note:

- Ostwald's dilution law is applicable only for weak electrolytes but fails completely in the case of strong electrolytes.
- All salts (except $CdBr_2$, $HgCl_2$) mineral acids like HCl , H_2SO_4 , HNO_3 etc., and bases like $NaOH$, KOH etc., are strong electrolytes.
- All organic acids (except sulphonic acids), inorganic acids like HCN , H_3BO_3 etc., and bases like NH_3 , amines etc., are weak electrolytes.
- In case of an acid, number of ionisable protons per molecule of acid is called its basicity. Similarly, in case of base, number of ionisable hydroxyl ions per molecule of base is called its acidity.

21. Ionic product of water

Water is amphiprotic and gives H^+ and $[OH^-]$ on self ionisation.

Ionic product of water, $K_w = [H^+][OH^-] = 10^{-14}$ at $25^\circ C$.

It depends only on temperature. It increases with increase in temperature.

Ionic product of water, K_w like all equilibrium constants varies with temperature. It increases with increase in temperature. For example $K_w \approx 10^{-15}$ at $273 K$, $K_w \approx 10^{-14}$ at $298 K$ and $K_w \approx 10^{-13}$ at $333 K$, therefore, at $273 K$ a neutral solution has a $pH = 7.5$ and at $298 K$ a neutral solution has a $pH = 7$. At 60° , the neutral solution has a pH of 6.5 instead of 7.0 and that pH scale lies between 0 and 13 . Thus, we find that pH decreases with increases

in temperature. At a temperature of human body ($\approx 37^\circ C$) pH of a neutral solution is 6.8 and pH scale lies between 0 and 13.6 .

22. pH value

$$pH = -\log [H_3O^+]$$

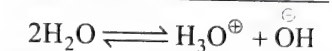
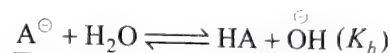
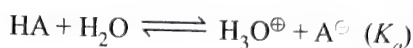
$$\text{or } [H_3O^+] = 10^{-pH}$$

$$\text{Similarly, } pOH = -\log [OH^-]$$

$$[OH^-] = 10^{-pOH}$$

$$\text{And, } pH + pOH = pK_w = 14 \text{ at } 25^\circ C$$

For conjugate acid-base pair in aqueous solution, i.e., HA and A^-



$$\text{Thus, } K_w = K_a \times K_b$$

$$\text{And } pK_a + pK_b = pK_w = 14 \text{ at } 25^\circ C$$

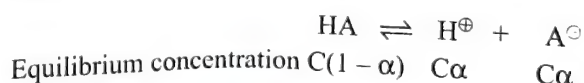
Higher the pK_a value, lower is the acid strength and higher is the basic strength.

- A solution having $pH = 0$ is acidic.
- pH of a solution decreases on heating as the dissociation of water is an endothermic process.
- pH values greater than 14 are possible for concentrated strong base and negative pH values are possible for concentrated strong acids, but it is for dilute solutions that pH scale is more useful.
- pH of solutions of acids, bases and salts of same concentration varies from one another. It depends on the extent to which a particular substance ionises in solution.
- pH of solutions can be determined accurately by pH meter or by e.m.f. method or roughly by universal indicator or pH paper.
- pH of boiling water is 6.5 although it is neutral.
- The word p in pH stands for French word *puissance* or German word *potenz* means power.
- For strong acids/bases, normality is taken directly as H^+ ion and OH^- ion concentration. If molarity is given, convert it into normality.

$$\text{Normality (N)} = \frac{\text{Molarity (M)} \times \text{Molecular weight}}{\text{Equivalent weight}} \quad (\text{OR})$$

$$N = "n" \text{ factor} \times M$$

- For a weak acid/base the pH shall depend on its degree of ionisation. For example, pH of weak acid HA is given as:



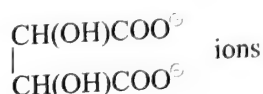
Here $[H^+] = C\alpha \therefore pH = -\log [C\alpha]$

Also since K_a of weak acid $= C\alpha^2$

$$\frac{K_a}{\alpha} = C\alpha = [H^+]$$

Hence $pH = \log \frac{K_a}{\alpha}$

- j. pH values do not give instantaneous idea about the relative strengths of the solution e.g., A 4×10^{-5} N HCl is twice concentrated as compared to 2×10^{-5} N HCl, but the pH values of these are 4.40 and 4.70 (not double).
- k. pH values is zero for 1 N solution of strong acid. In case of 2N, 3N, 4N etc., solutions, pH values are negative.
- l. pH range for some important substance are:
- | | | | |
|---------------|-----------|--------------|-------------|
| Gastric juice | 1.0 – 3.0 | Soft drinks | 2.0 – 4.0 |
| Vinegar | 2.4 – 3.4 | Human urine | 4.8 – 8.4 |
| Human saliva | 6.5 – 7.5 | Blood plasma | 7.36 – 7.42 |
| Tears | 7.4 | | |
- m. The relationship between pH and hydrogen ion concentration is inverse one. Thus as pH goes up hydrogen ion concentration goes down.
- n. the relationship between pH and hydrogen ion concentration is also logarithmic one. For example decrease of pH by one unit, corresponds to ten fold increase in hydrogen ion concentration. Similarly, when pH goes down by two units, hydrogen ion concentration increases by a factor of 100.
- o. K_w value does not change on the addition of a salt, acid or base at a particular temperature.
- p. Degree of ionisation of pure water is 1.8×10^{-9} or $1.8 \times 10^{-7}\%$ at 25°C which indicates that it is a very weak electrolyte.
- q. pH relates to negative power of 10. Hence, a solution of $pH = 1$ has hydrogen ion (or hydronium ion) concentration 100 times that of a solution of $pH = 3$ (not three times).
- r. Since pH is related to a negative exponent, the lower the pH value, the larger the concentration.
- s. pH of a buffer changes with temperature because K_w changes with temperature.
- t. Mixed salts give more than one cation or anion on dissolving in water. For example,
- Bleaching powder, CaOCl_2 gives Ca^{2+} , OCl^- and Cl^-
 - Rochelle salt (sodium potassium tartarate) gives Na^+ , K^+ and tartarate,



- u. Solubility of AgCl in NaCl solution is less than that in water because $[\text{Cl}^-]$ increases so that $[\text{Ag}^+]$ decreases due to common ion effect.
- v. A solution of an acid having very low concentration (e.g., 10^{-8} M HCl) cannot have pH 8, as given by pH formula but the actual pH value will be less than 7. pH of any acid can never be greater than 7. For example, 10^{-8} M HCl has a $pH = +6.958$. In such cases as the H^+ ion concentration of acid is less than that originally present in water, therefore H^+ conc. of water is also taken into account.

$$\begin{aligned} \text{Total } \text{H}^+ \text{ ion concentration} &= 10^{-8} + 10^{-7} = \\ &= 10^{-8} [1 + 10] = 11 \times 10^{-8} \end{aligned}$$

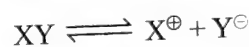
$$pH = -\log 11 \times 10^{-8} = 6.958$$

For 10^{-8} M NaOH solution pH is not 6, because basic solution always leave $pH > 7$. This solution has $pH = 7.04$

23. Common ion effect

The degree of dissociation of a weak electrolyte is suppressed by the addition of another strong electrolyte containing common ion. It is called common ion effect.

In case of weak electrolyte,



$$K = \frac{[X^+][Y^-]}{[XY]}$$

In case any other strong electrolyte containing X^+ or Y^- ions is added, the equilibrium tends to shift to left in order to keep K constant at given temperature, i.e., $[\text{H}^+]$ in solution decreases or $[XY]$ increases or in other words the degree of dissociation of HX decreases.

Note: In presence of a common ion (from strong electrolyte) present with weak electrolyte, the concentration of common ion is derived from strong electrolyte.

- At half neutralisation point of weak acid where $[\text{HA}] = [\text{A}^-]$
 $pH = pK_a$
 $[\text{H}^+] = K_a$
- At half neutralisation point of weak base where $[\text{BOH}] = [\text{B}^+]$
 $\therefore pOH = pK_b$
 $[\text{OH}^-] = K_b$
 $\therefore pH = 14 - pK_b$
- In case of weak dibasic acid (e.g., H_2CO_3), pH at half neutralisation point is

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

24. **Buffer solution:** A solution that resists change of pH upon the addition of small amount of acid or alkali.

a. **Simple buffer:** Salts of weak acid and weak base, e.g., $\text{CH}_3\text{COONH}_4$, NH_4CN , etc.

b. **Acid buffer**

They are prepared by mixing weak acid and its salt with strong base or it contains a weak acid and its conjugate base, e.g., CH_3COOH and CH_3COONa .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

c. **Basic buffer:** These are prepared by mixing weak base and its salt with strong acid or it contains a weak base and its conjugate acid, e.g., NH_4OH and NH_4Cl .

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

d. **Salt buffer:** It is a salt of weak acid and weak base.

$$[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

e. **Buffer range:**

i. An acidic buffer is effective within pH range ($\text{p}K_a - 1$) to ($\text{p}K_a + 1$).

ii. A basic buffer is effective in pH range ($\text{p}K_b - \text{p}K_b \pm 1$).

iii. pH of a buffer does not change on dilution.

f. **Buffer capacity:**

$$\text{Buffer capacity} = \frac{\text{Number of moles of acid or base added per litre}}{\text{Change in pH}}$$

It is maximum when

$$\text{For acidic buffer, } \frac{[\text{salt}]}{[\text{acid}]} = 1; \quad \text{pH} = \text{p}K_a$$

$$\text{For basic buffer, } \frac{[\text{salt}]}{[\text{Base}]} = 1; \quad \text{pOH} = \text{p}K_b$$

Note:

1. A nearly constant pH is maintained by buffers when diluted with water or dilute acid or base is added.
2. Buffer capacity is largest when the concentration of a salt and weak acid/base are equal or when $\text{pH} = \text{p}K_a$.
3. pH of buffer depends on concentration ratio of the base to salt.
4. pH of a buffer varies with temperature because K_w value changes with temperature.
5. Simple buffers. Buffer solutions can also be prepared by (a) a solution of ampholytes, e.g. proteins and amino acids. (b) a mixture of an acid salt and a normal salt of polybasic acid, e.g., $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$ or a salt of weak acid and a weak base such as $\text{CH}_3\text{COO}_3\text{NH}_4$, NH_4CN , etc.
6. Buffer solutions have reserve acidity and reserve alkalinity.
7. The greater the buffer capacity, the greater is its capacity to resist change in pH value.
8. Buffers cannot withstand the addition of large amounts of acids or alkalis. The addition of 0.01 mol per litre of H^+ or OH^- is about the maximum that any buffer can be expected to withstand.

III. Salt hydrolysis (for uni-univalent salts)

S. No.	Salt	Nature	Hydrolysis Constant	Degree of Hydrolysis	$[\text{H}_3\text{O}^+]$	pH
1.	Salt of strong acid and strong base, e.g., NaCl , KCl	Neutral	—	No hydrolysis	—	7
2.	Salt of weak acid and strong base, e.g., CH_3COONa	Basic	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a C}}$	$\sqrt{\frac{K_w K_a}{C}}$	$\text{pH} = \frac{\text{p}K_w + \text{p}K_a + \log C}{2}$
3.	Salt of weak base and strong acid, e.g., NH_4Cl	Acidic	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b C}}$	$\sqrt{\frac{K_w}{K_b C}}$	$\text{pH} = \frac{\text{p}K_w - \text{p}K_b - \log C}{2}$
4.	Salt of weak acid and weak base	May be acidic, basic, or neutral	$K_h = \frac{K_w}{K_a \times K_b}$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$\sqrt{\frac{K_w K_a}{K_b}}$	$\text{pH} = \frac{\text{p}K_w + \text{p}K_a - \text{p}K_b}{2}$

Note: For other types of salts say uni-bivalent e.g., $\text{Na}_2\text{C}_2\text{O}_4$ or bi-bivalent CaC_2O_4 , other equations are derived.

Note: In case of salt of weak acid and weak base, nature of medium will be (i) neutral if $K_a = K_b$, (ii) basic if $K_b > K_a$, and (iii) acidic if $K_a > K_b$.

a. Hydrolysis is the reverse of neutralisation.

b. It should be noted that, in salt hydrolysis

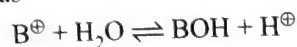
$$\text{When } K_a = K_b, \text{pH} = 7$$

$$K_a > K_b, \text{pH} < 7$$

$$K_a < K_b, \text{pH} > 7$$

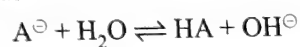
where K_a and K_b are the dissociation constants of acid and base formed during the hydrolysis of the salt.

c. **Cationic hydrolysis:** It is the hydrolysis reaction due to interaction of the cation of the salt with water. It is represented as



Salts of a strong acid and a weak base undergo cationic hydrolysis.

d. **Anionic hydrolysis:** It is the hydrolysis reaction due to interaction of the anion of the salt with water. It is represented as



Salts of a weak acid and strong base undergo anionic hydrolysis.

e. The net effect of dissolving a salt (which undergoes hydrolysis) is to break up the water molecules (hydrolysis) to produce weak acid to weak base or both and thus phenomenon is always endothermic.

f. The acid salts are more soluble than neutral salts e.g., $Ca_3(PO_4)_2$ is insoluble in water, $CaHPO_4$ is sparingly soluble but $Ca(H_2PO_4)_2$ is fairly soluble.

g. Salt hydrolysis affects the pH of the solution.

h. Degree of hydrolysis of a salt depends upon temperature and concentration. It increases with increase in temperature and decreases with increases in concentration and vice versa.

26. Isohydric solution

These are the solutions of the weak electrolytes containing equal concentration of the common ions present in them. When such solutions are mixed, no change in the degree of dissociation of either of the electrolyte occurs.

27. In the hydrolysis of salts of strong base and weak acid:

- anion of the salts is hydrolysed,
- free OH^{\ominus} ions are formed. The number of OH^{\ominus} ions formed, per molecule of the salts, due to hydrolysis is equal to the charge on the anion.
- greater the charge on anion greater the number of OH^{\ominus} ions produced due to hydrolysis hence greater the pH.

28. In the hydrolysis of salts of weak base and strong acid:

- cation of the salt is hydrolysed.
- free H_3O^{\oplus} (or H^{\oplus}) ions are formed. Number of H_3O^{\oplus} ions formed per molecule of salt, due to hydrolysis is equal to charge on the cation.

c. greater the charge, greater the number of H^{\oplus} ions formed due to hydrolysis, hence lower the pH.

29. There is no effect of dilution on the hydrolysis of salts of weak acid and weak base. This is because in this case h (degree of hydrolysis), pH and K_h are all independent of concentration C .

30. Salts of strong acids and strong bases (e.g., NaCl, KCl, KNO_3 etc.) do not undergo hydrolysis. The reason is that the possible products of hydrolysis are strong electrolytes and themselves get fully ionized. Such a solution is neutral i.e., its pH is 7.

31. a. Sparingly soluble salts and precipitation:

- Solution of a sparingly soluble salt is expressed in mol L^{-1} or g L^{-1} .
- Solubility (in mol L^{-1}) of any salt A_xB_y in pure water is given by:

$$\text{Solubility} = \left[\frac{(K_{sp})}{x^x \cdot y^y} \right]^{1/(x+y)}$$

- Solubility of a salt decreases in the presence of a common ion.

In general, we can neglect the contribution of common ion from the sparingly soluble salt.

e.g., solubility of AgCl in x M NaCl

$$= \frac{K_{sp} \text{ AgCl}}{[Cl^{\ominus}]} = \frac{K_{sp} \text{ AgCl}}{x}$$

b. **Selective precipitation:** When difference in the minimum concentrations of common cation/anion required to start the precipitation is very high.

To check, always calculate the concentration of the cation/anion left in the solution when the second cation/anion starts to precipitate, and so on.

c. **Simultaneous solubility:** Solubility of two or more salts having a common cation/anion when their K_{sp} values are comparable. Solve the governing equations simultaneously.

d. Precipitation of salts:

- If ionic product (IP or Q_{sp}) $> K_{sp}$, precipitation takes place till IP equals K_{sp} .
- If $IP < K_{sp}$, precipitate will not be formed.
- If $IP = K_{sp}$, precipitate will not be formed but the solution is at saturation stage.

32. Solubility of a sparingly soluble salt in the presence of common ion (when K_{sp} is very small)

Types of sparingly soluble salt	Common ion added	S in H_2O (Solubility) ($S_{initial}$)	S is common ion. (S_{new})
1. For uni-univalent type (e.g., AgCl) or For bi-bivalent type (e.g., $BaSO_4$)	Either cation or anion (e.g., Ag^+ or Cl^-) Ba^{2+} ion or SO_4^{2-} ion	$K_{sp} = S^2$ $S_{H_2O} = (K_{sp})^{1/2}$ common ion added.	$S_{new} = K_{sp}/(C)^n$ C = concentration of n = number of common ion in sparingly soluble salts.
2. For bi-univalent type e.g., $Ni(OH)_2$	Anion (OH^- ion)	$K_{sp} = 4S^3$ $S_{H_2O} = \left(\frac{K_{sp}}{4}\right)^{1/3}$	$S_{new} = \frac{K_{sp}}{(C)^n} = \frac{K_{sp}}{(C)^2}$
	Cation (Ni^{2+} ion)		$S_{new} = \left(\frac{K_{sp}}{4 \times C}\right)^{1/2}$
3. For uni-bivalent type e.g., $Ag_2C_2O_4$	Cation (Ag^+ ion)	$S_{H_2O} = \left(\frac{K_{sp}}{4}\right)^{1/3}$	$S_{new} = \frac{K_{sp}}{(C)^n} = \frac{K_{sp}}{(C)^2}$
	Anion ($C_2O_4^{2-}$ ion)		$S_{new} = \left(\frac{K_{sp}}{4 \times C}\right)^{1/2}$
4. For tri-univalent type e.g., $Al(OH)_3$	Anion (OH^- ion)	$K_{sp} = 27S^4$ $S_{H_2O} = \left(\frac{K_{sp}}{27}\right)^{1/4}$	$S_{new} = \frac{K_{sp}}{(C)^n} = \frac{K_{sp}}{(C)^3}$
	Cation (Al^{3+} ion)		$S_{new} = \left(\frac{K_{sp}}{27 \times C}\right)^{1/3}$

33. Theory of indicator

- Transition range of an indicator: ($pK_{Ind} - 1$) to ($pK_{Ind} + 1$).
- For S_A/S_B titration, almost every indicator is effective.
- For S_A/W_B and W_A/S_B indicator, selection is important and depends on the pH at equivalence point.

- Ostwald's theory:** Indicators are generally weak organic acids or bases. The unionised and ionised form of indicators have different colours. They change colours within certain pH range and are used for the determination of end point in the titrations.



$$K_{Ind} = \frac{[H_3O^+][Ind^-]}{[HIn]}$$

K_{Ind} depends only on temperature.

$$[H_3O^+] = K_{ind} \frac{[HIn]}{[Ind^-]}$$

$$\text{Thus, } pH = pK_{ind} + \log \frac{[Ind^-]}{[HIn]}$$

$pH \leq pK_{Ind} - 1$, the solution has a characteristics colour of HIn.

$pH \geq pK_{Ind} + 1$, the solution has a characteristic colour of Ind^- .

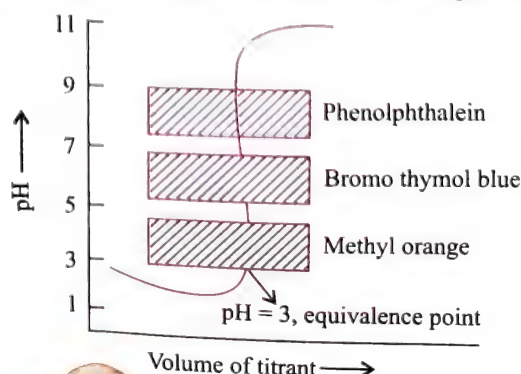
- Equivalence point:** At equivalence point, the pH value of the solution, that is under going titration, changes steeply and pH range of this steep change depends on the nature of acid-base pair being titrated.

At equivalence point, $[Ind^-] = [HIn]$

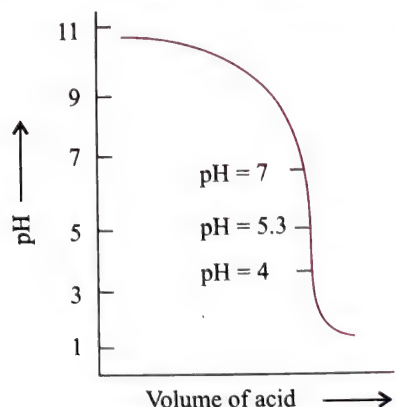
$$pH = pK_{Ind} \text{ or } [H^+] = K_{ind}$$

- Selection of suitable indicator:** The indicator should offer a colour change at equivalence point or the pH transition range of the indicator must coincide with the steep portion of the titration curve.

34. Titration of strong acid (HCl) and strong base (NaOH)

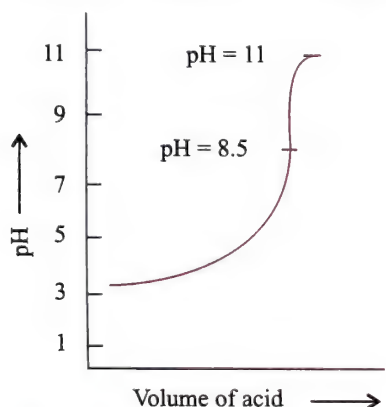


35. Titration of weak base (NH_4OH) and strong acid (HCl)



Methyl red and methyl orange can be used, phenolphthalein cannot be used.

Titration of weak acid (CH_3COOH) and strong base (NaOH):



Phenolphthalein is a suitable indicator

Note:

- At the equivalence point $pK_{\text{indicator}} = \text{pH}$. However, indicators have a useful colour change over pH range of 2 units.

Thus,

$$\text{pH} = pK_{\text{indicator}} \pm 1$$

- At half of the equivalence point of an acid, i.e. the point at which half of the acid has been neutralised

$$\text{pH} = pK_a$$

Similarly, at half neutralisation of a base

$$\text{pOH} = pK_b$$

36. Solubility of a salt of weak monoprotic acid in presence of H^+ ion from buffer solution

The solubility of salts of weak acid increases with increase in $[\text{H}^+]$ or increases at lower pH. For example, the solubility of CH_3COOAg in buffer solution is given by the formula. (K_a is the dissociation constant of weak monoprotic acid, K_{sp} is the solubility product of salt)

$$S \text{ in buffer} = \left[K_{\text{sp}} \left(1 + \frac{[\text{H}^+]}{K_a} \right) \right]^{1/2}$$

$$S \text{ in } \text{H}_2\text{O} = \sqrt{K_{\text{sp}}}$$

The ratio of solubilities of salt in presence of buffer and in water is

$$\frac{S \text{ in buffer}}{S \text{ in } \text{H}_2\text{O}} = \left(1 + \frac{[\text{H}^+]}{K_a} \right)^{1/2}$$

37. Miscellaneous

- For dissociation of H_2A , $[\text{A}^{2-}] \approx K_2$;

For H_3A $[\text{A}^{3-}] \approx K_3$ and so on.

- For a polyprotic acid, $K_{a1} \gg K_{a2} \gg K_{a3}$ and so on.
- Solubility of a salt can be increased by adding a substance that makes a stable complex/compound with any of the cation/anion in the salt.

e.g., AgCl dissolves more in aqueous NH_3 solution due to the formation of $\text{Ag}(\text{NH}_3)_2^+$ and AgCN dissolves more in an acidic solution due to the formation of HCN (weak electrolyte).

- The pH of acidic salt in water of polyprotic acid (e.g., NaHS) and of zwitter ion (e.g., $\text{NH}_3^+ \text{CH}_2\text{COO}^-$) is given by:

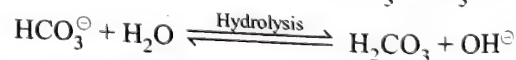
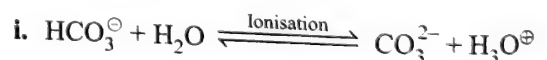
$$\text{pH} = \left(\frac{pK_{a1} + pK_{a2}}{2} \right)$$

38. Some additional examples of buffers: Following are some more examples of simple buffers.

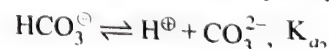
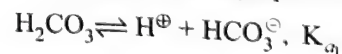
- A salt of a weak acid and weak base in water e.g. $(\text{NH}_4)_2\text{CO}_3$, $\text{CH}_3\text{COONH}_4$, NH_4CN etc.
- Proteins and amino acids.
- A mixture of a normal salt and an acid salt of a polybasic acid e.g., NaHCO_3 and Na_2CO_3 ; Na_2HPO_4 and Na_3PO_4 etc.

39. a. Hydrolysis of amphiprotic anions (cation not hydrolysed). Acid salts of weak acid and strong base like NaHCO_3 , NaHS etc., can undergo ionisation to form H^+ ions and can also undergo hydrolysis to form OH^- (Na^+ ion is not hydrolysed)

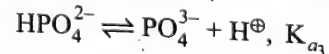
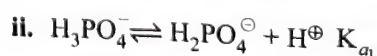
For example,



Thus H_2CO_3 is amphiprotic anion



$$\text{pH} = \frac{1}{2} [pK_{a1} + pK_{a2}]$$



$$\text{pH}(\text{H}_2\text{PO}_4^-) = \frac{1}{2} [pK_{a1} + pK_{a2}]$$

$$\text{pH}(\text{HPO}_4^{2-}) = \frac{1}{2}[\text{p}K_{a_2} + \text{p}K_{a_3}]$$

b. Hydrolysis of amphiprotic anion (cation is also hydrolysed)

In salts like $\text{NH}_4^+\text{HCO}_3^-$, NH_4^+HS^- etc., in which HCO_3^- , HS^- are amphiprotic and NH_4^+ ion is also hydrolysed, the $[\text{H}^+]$ can be calculated as

$$[\text{H}^+] = \sqrt{K_{a_1} \left[\frac{K_w}{K_b} + K_{a_2} \right]}$$

40. a. Hydrolysis constant of a salt of weak acid and strong base is the ionisation constant of the conjugate base of the weak acid.
- b. Hydrolysis constant of salt of a weak base and strong acid is the ionisation constant of the conjugate acid of the weak base.

8.1 INTRODUCTION

The type of equilibrium studied in chemical equilibrium is known as *molecular equilibrium* in which only the involvement of molecules takes place. There are various equilibria that involve ions only. This type of equilibrium involving ions in aqueous solution is called *ionic equilibrium*.

Aqueous solution of sugar does not conduct electricity; however, aqueous solution of NaCl (common salt) conducts electricity. Also, the conductance of electricity increases with an increase in concentration of NaCl.

Michael Faraday classified the substances into two categories based on their ability to conduct electricity.

- The substances which conduct electricity in their aqueous solutions are called electrolytes.
- The substances which do not conduct electricity in their aqueous solutions are called non-electrolyte.

Faraday further classified electrolytes into *strong* and *weak electrolytes*.

Strong electrolytes on dissolution in water are ionised almost completely while the *weak electrolytes* are only partially dissociated. For example, an aqueous solution of NaCl comprises entirely Na^+ ions and Cl^- ions, while that of acetic acid (CH_3COOH) mainly contains unionised acetic acid molecules and only some acetate ions (CH_3COO^-) and H^+ ions. This is because NaCl is 100% ionised while CH_3COOH is ionised less than 5% since it is a weak electrolyte.

In weak electrolytes, equilibrium is established between ions and unionised molecules. Such type of equilibrium involving ions in aqueous solution is called *ionic equilibrium*.

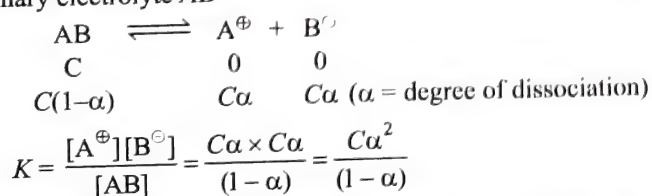
Ions in solution are formed mainly from two ways:

- When solute is ionic compound, i.e., strong electrolyte, e.g., NaCl, MgCl_2 , KCl, KBr, KNO_3 , NaOH, and KOH. In such compounds, ions maintain their identity even in solid state. On dissolution in water, ions get separated and ionisation is almost 100% complete.
- When the solute is polar covalent compound and reacts with H_2O to form ions. These may be strong or weak electrolytes depending upon their respective degree of ionisation (α), e.g., H_2SO_4 , HNO_3 , HCl, NH_3 , CH_3COOH , HCN, NH_4OH , etc.

$$\text{c. Degree of ionisation } (\alpha) = \frac{\text{Number of moles dissociated}}{\text{Total number of moles taken}}$$

8.2 OSTWALD'S DILUTION LAW

The application of law of mass action to weak electrolytes is known as Ostwald dilution law. There exists dynamic equilibrium between ions and undissociated molecules of the electrolytes in solution and the law of mass action can be applied to this. Consider a binary electrolyte AB



K is termed as ionisation constant. For a weak electrolyte, value of α is very small compared to 1 and $(1-\alpha) \approx 1$.

$$\therefore K = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha \propto \frac{1}{\sqrt{C}}$$

If V be the volume of the solution containing 1 mol of solute, then $C = \frac{1}{V}$.

Hence $\alpha = \sqrt{KV}$ or $\alpha \propto \sqrt{V}$ as ionic equilibrium is set up in case of weak electrolytes. Ostwald's dilution is applicable only in case of weak electrolytes.

The approximation $(1-\alpha) \approx 1$ can be applied only if $\alpha < 5\%$. If on solving a problem by applying the approximate formula; α comes out to be $>5\%$, the problems may be solved by applying the exact formula and α may be calculated applying the solution of the quadratic equation

$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{for, } a\alpha^2 + b\alpha + c = 0)$$

8.3 ACIDS, BASES, AND SALTS

As most of the acids taste sour, the word *acid* has been derived from a Latin word *acidus* meaning sour. Acids turn blue litmus paper into red and liberate H_2 gas on reacting with metals. Similarly, bases turn red litmus paper blue, taste bitter and feel soapy.

HCl acid present in gastric juice is secreted by, the lining of our stomach in significant amount of $1.2\text{--}1.5 \text{ L day}^{-1}$ and is essential for digestive process. Acetic acid is the main constituent of Vinegar. Lemon and orange juice contains citric and ascorbic acid (vitamin C) and tartaric acid is found in tamarind paste

Similarly, a common example of a base is washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) used for washing purposes.

When acids and bases react in proper proportions, they give salts. Some examples of salts are: NaCl, BaSO_4 and NaNO_3 . NaCl (common salt) is an important constituent of our diet. It exists in solid state as a cluster of Na^+ and Cl^- ions held together by electrostatic interactions of oppositely charged species. (Fig. 8.1).

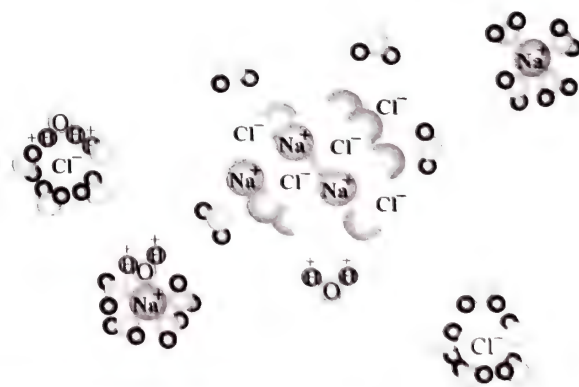


Fig. 8.1 Dissolution of NaCl in H_2O . Na^+ and Cl^- ions are stabilised by their hydration with polar H_2O molecules.

The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, has a very high dielectric constant of 80. Thus on dissolution of NaCl in H_2O . The electrostatic interaction are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Moreover, they are well-shaped due to hydration with water molecules.

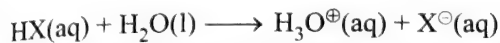
The extent of ionisation depends upon the strength of the bond and extent of solvation of ions produced. Although both HCl and CH_3COOH are polar covalent molecules, the HCl is completely ionised into the constituent ions, while the latter is only partially ionised (<5%).

8.3.1 ARRHENIUS CONCEPTS OF ACIDS AND BASES

According to Arrhenius theory, *acids are substances that dissociate in water to give $\text{H}^{\oplus}(\text{aq})$ ions and bases are substances that produce $\text{OH}^{\ominus}(\text{aq})$ ions*. The ionisation of an acid $\text{HX}(\text{aq})$ is shown as:

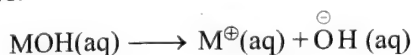


or



H^{\oplus} ions is a bare proton and is very reactive and does not exist freely in aqueous solutions. Thus, it combines with oxygen atom of a solvent water molecule to give trigonal pyramidal *hydronium* ion, $\text{H}_3\text{O}^{\oplus}$ $\{[\text{H}(\text{H}_2\text{O})]^{\oplus}\}$.

Similarly, a base molecule such as MOH ionises in aqueous solution as follows:

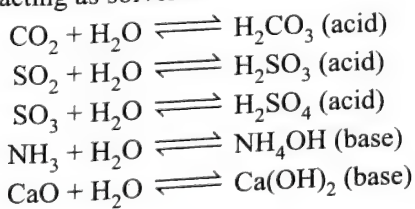


The OH^{\ominus} ions also exist in the hydrated form in the aqueous solutions.

8.3.2 LIMITATIONS OF ARRHENIUS CONCEPT

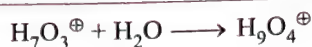
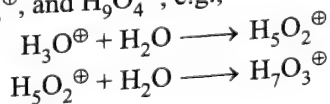
- It is applicable only to aqueous solutions and also does not account for the basicity of substances such as, NH_3 which does not have hydroxyl group.
- It fails to explain the acidic and basic character of the substance in solvents other than H_2O , such as liquid NH_3 , liquid SO_2 , and alcohol.
- According to Arrhenius concept an acid gives H^{\oplus} ions in water. But H^{\oplus} ion does not exist independently and combines with H_2O molecule to form hydronium ion ($\text{H}_3\text{O}^{\oplus}$).
- It fails to explain the acidic characters of certain substances such as CO_2 , SO_2 , and SO_3 , which do not have hydrogen atom. Similarly, it also fails to explain the basic characters of certain substances such as NH_3 , CaO and MgO , which do not have hydroxyl group.

However, this limitation can be overcome in the presence of water acting as solvent.

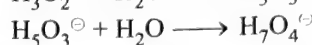
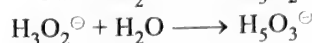
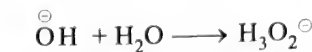


8.3.3 HYDRONIUM IONS AND HYDROXYL IONS

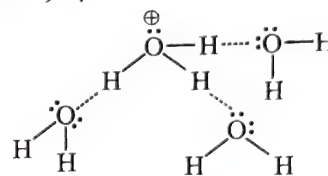
H^{\oplus} ion is a bare proton ($\sim 10^{-15}$ m radius) with intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving, and $\text{H}_3\text{O}^{\oplus}$. This species has been detected in many compounds (e.g., $\text{H}_3\text{O}^{\oplus}\text{Cl}^{\ominus}$) in the solid state. In aqueous solution the $\text{H}_3\text{O}^{\oplus}$ is further hydrated to give species such as $\text{H}_5\text{O}_2^{\oplus}$, $\text{H}_7\text{O}_3^{\oplus}$, and $\text{H}_9\text{O}_4^{\oplus}$, e.g.,



Similarly, the OH^{\ominus} ion is hydrated to give several ionic species such as $\text{H}_3\text{O}_2^{\ominus}$, $\text{H}_5\text{O}_3^{\ominus}$, and $\text{H}_7\text{O}_4^{\ominus}$.

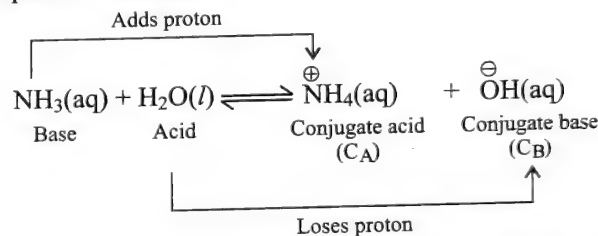


Structure of $\text{H}_9\text{O}_4^{\oplus}$



8.3.4 THE BRÖNSTED-LOWRY ACIDS AND BASES

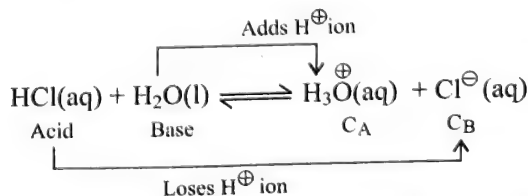
According to the Danish Chemist, Johannes Brønsted, and the English Chemist, Thomas M. Lowry, *acid is a substance that donates H^{\oplus} ions and bases are substances which accept H^{\oplus} ions*. In other words, acids are proton donor and bases are proton acceptors. For example,



In the above reaction, H_2O molecule acts as proton donor and NH_3 molecule acts as proton acceptor and thus is called Brønsted-Lowry acid and base, respectively. The solution is basic due to the presence of OH^{\ominus} ions. In the reverse reaction, H^{\oplus} ion is transferred from NH_4^{\oplus} to OH^{\ominus} , thus NH_4^{\oplus} acts as a Brønsted acid, while OH^{\ominus} acts as a Brønsted base. Such acid base pairs that differs only by one H^{\oplus} ion is called a *conjugate acid-base pair*. Therefore, OH^{\ominus} is called the conjugate base (C_B) of an acid H_2O and NH_4^{\oplus} is called the conjugate acid (C_A) of the base NH_3 . If Brønsted acid is a strong acid then its *conjugate base is a weak base and vice versa*. C_A has one extra H^{\oplus} ion and each C_B has one less H^{\oplus} .

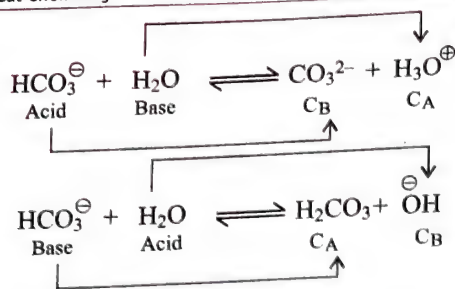
Ionisation of HCl in H_2O :

$\text{HCl}(\text{aq})$ acts as an acid by donating a H^{\oplus} to H_2O molecule which acts as a base.



Therefore, H_2O acts both as an acid and base. In case of NH_3 , with H_2O it acts as an acid by donating a H^{\oplus} ion while in case of HCl , water acts as a base by accepting H^{\oplus} ion. Hence H_2O acts as *amphiprotic*, i.e.,

Similarly, HCO_3^{\ominus} , HSO_4^{\ominus} , $\text{H}_2\text{PO}_4^{\ominus}$, HPO_4^{2-} , $\text{H}_2\text{PO}_3^{\ominus}$, HSO_3^{\ominus} are amphiprotic.



Thus, a substance which acts both an acid as well as a base in different reactions is called *amphiprotic*.

Table 8.1 Acid-base charge containing some conjugate acid-base pairs.

Acid	Conjugate base
HClO ₄ (Perchloric acid)	ClO ₄ [−] (Perchlorate ion)
H ₂ SO ₄ (Sulphuric acid)	HSO ₄ [−] (Hydrogen sulphate ion)
HCl (Hydrochloric acid)	Cl [−] (Chloride ion)
HNO ₃ (Nitric acid)	NO ₃ [−] (Nitrate ion)
H ₃ O ⁺ (Hydronium ion)	H ₂ O (Water)
HSO ₄ [−] (Hydrogen sulphate ion)	SO ₄ ^{2−} (Sulphate ion)
H ₃ PO ₄ (Ortho phosphoric acid)	H ₂ PO ₄ [−] (Dihydrogen phosphate ion)
CH ₃ COOH (Acetic acid)	CH ₃ COO [−] (Acetate ion)
H ₂ S (Hydrogen sulphide)	HS [−] (Hydrogen sulphide ion)
NH ₄ ⁺ (Ammonium ion)	NH ₃ (Ammonia)
HCN (Hydrogen cyanide)	CN [−] (Cyanide ion)
PhOH (Phenol)	PhO [−] (Phenoxide ion)
H ₂ O (Water)	OH [−] (Hydroxide ion)
C ₂ H ₅ OH (Ethanol)	C ₂ H ₅ O [−] (Ethoxide ion)
NH ₃ (Ammonia)	NH ₂ [−] (Amide ion)
CH ₄ (Methane)	CH ₃ [−] (Methinide ion)

8.3.5 LEWIS ACIDS AND BASES

G.N. Lewis, in 1923, defined an *acid* as a species which accepts electron pairs (or lone pairs) and base which donates an electron pairs.

For bases there is not much difference between Brønsted–Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton.

Thus, all Brønsted–Lowry bases are Lewis bases, while all Brønsted–Lowry acids are not Lewis acids.

For example, in the reaction between electron-deficient species BF₃ and NH₃, BF₃ does not have a proton but still acts as an acid and reacts with NH₃ by accepting its lone pair of electrons.



Lewis Acids

- Compounds where the central atom has incomplete octet. This means all electron-deficient molecules can act as Lewis

acids, e.g., BF₃, BBr₃, AlCl₃, FeCl₃, and GaCl₃

- Compounds in which the central atom has available vacant orbitals, e.g., SnF₄, SnCl₂, SnCl₄, PF₃, PF₅, SF₄, and TiCl₄
- Simple cations such as, Ag⁺, Cu²⁺, Al³⁺, Co³⁺ and Mg²⁺ e.g., Cu²⁺ + 4NH₃ → [Cu(NH₃)₄]²⁺
- Compounds which have multiple covalent bonds, e.g., CO₂ (O=C=O), CS₂ (S=C=S), SO₂ ($\text{S}=\text{O}$)

Under the influence of attacking Lewis base, one electron pair will be shifted towards more negative atom.



Lewis Bases

- All simple anions are Lewis bases, e.g., NO₃[−], Cl[−], OH[−].
- Molecules containing one or more unshared pairs of electrons (lone pairs), e.g., H₂O, NH₃, ROH, NX₃, and R₂S, are Lewis bases provided the octet of the central atom is complete.
- Multiple-bonded compounds which can donate the lone pair of electrons, e.g.,



8.3.6 FACTORS AFFECTING THE STRENGTH OF LEWIS ACIDS

- Nuclear charge on central atoms:
More the nuclear charge on central atom more the Lewis acidic strength.
- Number of electronegative (EN) atom attached to the central atoms:
More the number of EN atoms attached more is the acidic strength, e.g., SO₃ is more stronger acid than SO₂.
- Increase in positive charge on ion make it relatively a strong acid.
e.g., Sn⁴⁺ > Sn²⁺ (acidic strength)
Fe³⁺ > Fe²⁺ (acidic strength)
- When charge is same on the cation then the decrease in the radii of cation increases the acidic strength.
e.g., Li⁺ > Na⁺ > K⁺ (acidic strength)
- With increase in the nuclear charge, the acidic strength also increases.
e.g., Li⁺ < Be²⁺ < B³⁺

Note: All Brønsted bases are also Lewis bases but all Brønsted acids are not Lewis acids.

8.4 HARD AND SOFT ACIDS AND BASES (HSAB)

Lewis acids and bases are further classified as Hard acids, Hard bases and soft acids, soft bases.

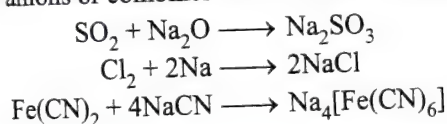
- a. Cations (electrons accepting atoms) having high charge, and small sizes are termed as hard acids, while cations (electron-accepting) atoms have less charge and large size are termed as soft acids.
- b. A Lewis base where the electrons can be easily polarised or where the base holds its electrons weakly is called soft base, while those lewis bases where the electrons are not easily polarised or where the base holds its electrons strongly are called hard bases.

Table 8.2 Examples of hard acids, hard bases and, soft acids, soft bases:

Hard acids	Hard bases	Soft acids	Soft bases
Li ⁺ , K ⁺ , Na ⁺ , Ca ²⁺ , Sr ²⁺ , Al ³⁺ , Fe ²⁺	H ₂ O, OH ⁻ , F ⁻ , Cl ⁻ , CO ₃ ²⁻ , CrO ₄ ²⁻ , NO ₃ ⁻ , NH ₃ , NH ₂ ⁻	Pb ²⁺ , Cd ²⁺ , Hg ²⁺ , GaCl ₃ , I ₂ , Br ₂	R ₂ S, R ⁻ , CN ⁻ , R ₃ P, I ⁻ , RNS, C ₂ H ₄ , CH ₂ =CH ₂
Ce ³⁺ , As ³⁺ , BF ₃ , SO ₃			

8.4.1 USANOVICH CONCEPT

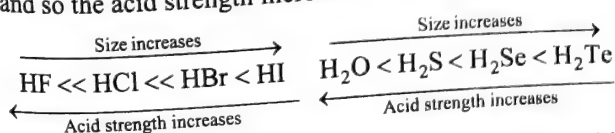
According to Usanovich, an acid is a chemical species which reacts with bases, gives up cations or accepts anions or electrons, and conversely a base is any chemical species which reacts with acids, gives up anions or combines with cation. For example,



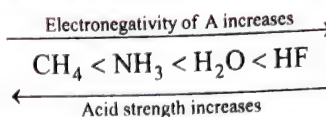
8.4.2 FACTORS AFFECTING ACID STRENGTH

Extent of dissociation of an acid depends on the *strength* and *polarity* of the H-A bond.

- a. In general when strength of an H-A bond decreases, i.e. the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar, i.e. electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.
- b. However, while comparing elements in the same group of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A strength decreases and so the acid strength increases. For example,



- c. For the elements in the same period of periodic table, H-A bond polarity decides the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,



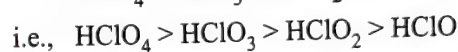
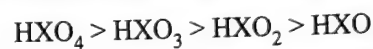
- d. For the elements of different group and different period, H-A bond strength decides the acid strength, weaker the H-A bond stronger the acid. For example,



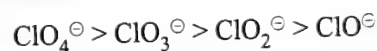
- e. For the oxo acids, HClO, HBrO, HIO, as the electronegativity of halogen increases, the strength of acid increases. For example,



- f. For the oxo acids, the acidic strength follows the order



This is because the conjugate base stability due to more resonating structure is



8.4.3 SALTS

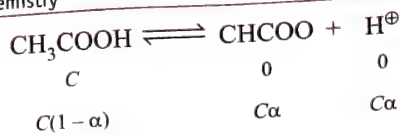
A substance which ionises in water to produce ions other than H⁺ than OH⁻ is called salt.

8.4.4 TYPES OF SALTS

- a. **Neutral salts:** Aqueous solutions of salts which neither turns blue litmus red nor red litmus blue are called neutral salts. These are prepared by the neutralisation of strong acid and strong base, e.g. NaCl, K₂SO₄, and KNO₃.
- b. **Basic salts:** Aqueous solutions of salts which turn red litmus blue are called basic salts. These are formed by the neutralisation of strong bases with weak acids, e.g., Na₂CO₃, and CH₃COONa.
- c. **Mixed salts:** Salts formed by the neutralisation of one acid by two bases or one base by two acids are called mixed salts, e.g., Ca(OCl)Cl.
- d. **Double salts:** A compound of two salts aqueous solution shows the tests for all constituent ions is called double salt, e.g.
- Mohr salt FeSO₄·(NH₄)₂SO₄·6H₂O
- Potash Alum K₂SO₄·Al₂(SO₄)₃·24H₂O.
- e. **Complex Salts:** A compound whose solutions does not give tests for the constituent ions is called a complex salt, e.g., K₄[Fe(CN)₆] and Li[AlH₄]

8.4.5 RELATIVE STRENGTH OF WEAK ACIDS AND BASES

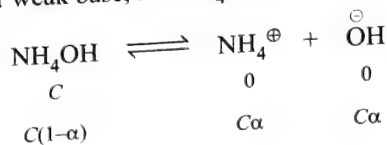
The relative strength of weak acids and bases are generally determined by their dissociation constants K_a and K_b , respectively. For weak acid, i.e. CH₃COOH



$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\Rightarrow K_a = C\alpha^2 \text{ (if } \alpha \ll 1)$$

Similarly for weak base, i.e. NH_4OH



$$K_b = C\alpha^2$$

K_a and K_b are the equilibrium constants and hence depend only on temperature. Greater the value of dissociation constant of the acid (K_a), more is the strength of the acid, and similarly, greater the value of dissociation constant base, more is the strength of the base. For two acids of equimolar concentrations

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

Similarly, for bases

$$\frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

The modern method is to convert K_a , as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit $\text{p}K_a$. Thus if K_a for acid is equal to 10^{-4} , $\text{p}K_a = 4$ so higher $\text{p}K_a$ value means lower acid strength,

$$\text{that is } \text{p}K_a = -\log K_a$$

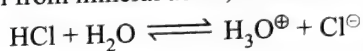
$$\text{Also, } \text{p}K_b = -\log K_b$$

8.5 CLASSIFICATION OF SOLVENTS

- Aprotic solvents**, which can neither accept nor donate a proton, e.g., CCl_4 , CS_2 , benzene.
- Amphiprotic solvents**, which can both accept and donate a proton, e.g., H_2O , liquid NH_3 .
- Protic solvents**, which have a greater tendency to accept proton, e.g., H_2O , $\text{R}-\text{OH}$, liquid NH_3 .

8.5.1 LEVELLING EFFECT

Water acts as a very strong base because it has a great tendency to accept proton from mineral acids, as shown:



Thus, all strong acids (e.g., HNO_3 , HCl , H_2SO_4 , HClO_4) react almost completely to form $\text{H}_3\text{O}^{\oplus}$ ion.

Therefore, all strong acids in aqueous solution appear equally strong, i.e. acidic level for all acids are same. This is called levelling effect and water is the levelling solvent. Thus, the relative

acidic strength or basic strengths in aqueous solutions cannot be compared.

When acetic acid is used as solvent instead of water, it is found that the acidic strength of acid lowers and now the given acid in acetic acid becomes weak and thereby different acids will dissociate to different extent in glacial acetic acid. This is because of poor proton-accepting character of acetic acid.

The acidic strength order is:

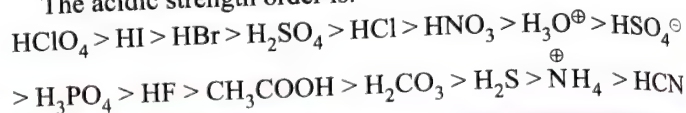


ILLUSTRATION 8.1

Write the conjugate bases for the following Brönsted acids.

- a. HF b. H_2SO_4 c. HCO_3^{\ominus}

Sol. C_B should have one H^{\oplus} ion less in each case and therefore the corresponding conjugate bases are:

- a. F^{\ominus} b. HSO_4^{\ominus} c. CO_3^{2-}

ILLUSTRATION 8.2

Write the conjugate acids for the following Brönsted bases.

- a. NH_2^{\ominus} b. NH_3 c. HCOO^{\ominus}

Sol. C_A should have one extra H^{\oplus} ion in each case and therefore the corresponding C_A are:

- a. NH_3 b. NH_4^{\oplus} c. HCOOH

ILLUSTRATION 8.3

The species H_2O , HCO_3^{\ominus} , HSO_4^{\ominus} , NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Sol.

	Species	C_A	C_B
i.	H_2O	$\text{H}_3\text{O}^{\oplus}$	OH^{\ominus}
ii.	HCO_3^{\ominus}	H_2CO_3	CO_3^{2-}
iii.	HSO_4^{\ominus}	H_2SO_4	SO_4^{2-}
iv.	NH_3	NH_4^{\oplus}	NH_2^{\ominus}

ILLUSTRATION 8.4

Classify the following species into Lewis acid and Lewis base and show how these act as such.

- a. OH^{\ominus} b. F^{\ominus} c. H^{\oplus} d. BCl_3

Sol.

- a. :OH^{\ominus} is a Lewis base as it can donate an electron pair.
 b. $(\text{:F})^{\ominus}$ ion acts as Lewis base as it can donate any one of its 4 lone pairs.

- c. H^+ ion is Lewis acid as it can accept a lone pair of electrons from bases such as OH^- and F^- ions.
- d. BCl_3 acts as Lewis acid as it can accept a lone pair of electrons from species such as NH_3 or $R-NH_2$ (amine) molecules.

ILLUSTRATION 8.5

- (i) In the reaction of BeF_2 with $2F^-$ to form BeF_4^{2-} , which reactant is the Lewis acid and which is the Lewis base?
- (ii) Write the conjugate bases of the following acids.
- HCN
 - $N_2H_5^+$
 - C_2H_5OH
 - HCO_3^-
- (iii) Write the conjugate acids of the following bases.
- C_5H_5N
 - $N_2H_5^+$
 - HCO_3^-
 - CH_3COOH
- (iv) Liquid NH_3 , like water, is an amphoteric solvent. Write the equation for the auto-ionisation of NH_3 .

Sol.

- (i) BeF_2 is the Lewis acid since it can accept lone pair of electrons from $:F^-$, and F^- is the Lewis base.
- (ii) In each case, the C_B is derived from the acid by loss of a proton.
- CN^-
 - N_2H_4
 - $C_2H_5O^-$
 - CO_3^{2-}
- (iii) In each case, the C_A is formed from the base by the addition of a proton.
- $C_5H_5NH^+$
 - $N_2H_6^{2+}$
 - H_2CO_3
 - $CH_3COOH_2^+$

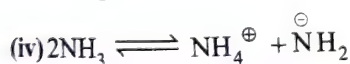


ILLUSTRATION 8.6

Aniline ($C_6H_5NH_2$) is a weak organic base in aqueous solution. Suggest a solvent in which aniline would become a strong base.

Sol. A solvent is needed which has appreciably stronger acid properties than H_2O ; one such solvent is liquid acetic acid (CH_3COOH).

ILLUSTRATION 8.7

Would each of the following ions in solution tend to produce an acidic, basic, or a neutral solution?

- CH_3COO^-
- Na^+
- SO_3^{2-}
- F^-
- NH_4^+

Sol.

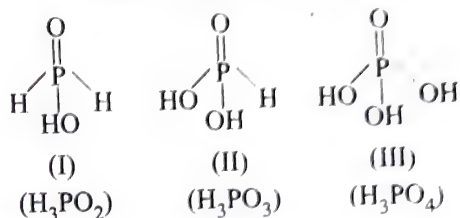
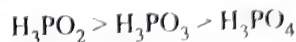
Note: Weaker is acid or base, stronger will be its conjugate basis or acid.

- (a., c. and d) are basic. Each is the conjugate of a weak acid
- b. is neutral it is the conjugate of a strong base
- e. is acidic, it is the conjugate of a weak base.

ILLUSTRATION 8.8

There is a little difference in acid strength of H_3PO_4 , H_3PO_3 and H_3PO_2 . Explain.

Sol. In general, with increase in oxidation number, acidic strength of oxyacids of both metals and non-metals, increases except in the acidic strength of oxyacids of phosphorous



This is due to the fact that the number of P-OH group per P = O increases from one in H_3PO_2 to 2 in H_3PO_3 and 3 in H_3PO_4 . The P-H bond is almost non-polar. The polar nature of $\overset{+8}{P}=\overset{-8}{O}$ group polarises the P-OH bonds. Therefore as the number of P-OH bonds increases, acidic strength decreases slightly. Moreover the electronegativities of P and H are almost same, thus P-H bond is not polarised. Hence no great differences in acidic strengths are expected.

ILLUSTRATION 8.9

The self ionisation constant for $HCOOH$ is 10^{-6} what percentage of $HCOOH$ are converted to $HCOO^-$ ion. The density of $HCOOH$ is 1.22 g mL^{-1} .

Sol.

$$\begin{aligned} \text{Mw of HCOOH} &= 46.0 \text{ g} \\ \text{Mass of HCOOH} &= V \times d = 1 \text{ mL} \times 1.22 \text{ g} \\ \text{Mass of HCOOH per L} &= 1.22 \text{ g} \times 10^3 \text{ mL} \\ &= 1220 \text{ g.} \end{aligned}$$

$$\begin{aligned} \text{Moles of HCOOH} &= \frac{\text{Mass}}{\text{Mw}} \\ &= \frac{1220 \text{ g L}^{-1}}{46.0 \text{ g}} \end{aligned}$$

$$= 26.5 \text{ mol L}^{-1} = 26.5 \text{ M}$$



$$K_a = [HCOO^-][HCOOH_2^+]$$

$$10^{-6} = [HCOO^-][HCOOH_2^+]$$

Since each ion is produced in equal number of moles
Therefore,

$$[HCOO^-] = [HCOOH_2^+] = 10^{-3} \text{ M}$$

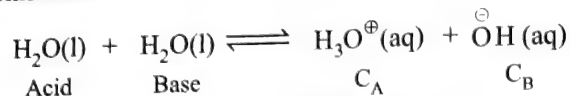
% dissociated to $HCOO^-$ ion

$$\begin{aligned} &= \left(\frac{10^{-3} \text{ M}}{26.5 \text{ M}} \right) \times 100 \\ &= 0.004\% \end{aligned}$$

8.6 IONISATION OF ACIDS AND BASES

8.6.1 THE IONISATION CONSTANT OF WATER AND ITS IONIC PRODUCT

H_2O is amphiprotic and gives $\text{H}_3\text{O}^{\oplus}$ and OH^{\ominus} as a result of self-ionisation.



The dissociation constant is represented by:

$$K = \frac{[\text{H}_3\text{O}^{\oplus}][\text{OH}^{\ominus}]}{[\text{H}_2\text{O}]^2}$$

The concentration of H_2O is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[\text{H}_2\text{O}]$ is incorporated with in the equilibrium constant to give a new constant, K_w , which is called the ionic product of water, (or auto protolysis constant) which increases with the increase of temperature.

$$\therefore K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^{\oplus}][\text{OH}^{\ominus}]$$

$$K_w = [\text{H}_3\text{O}^{\oplus}][\text{OH}^{\ominus}]$$

The concentration of $[\text{H}^{\oplus}] = [\text{OH}^{\ominus}] = 1.0 \times 10^{-7} \text{ M}$ at 298 K.

Thus, the value of K_w at 298 K.

$$K_w = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2.$$

$$-\log K_w = \text{p}K_w = -\log(10^{-14}) = 14$$

$$\therefore \text{p}K_w = 14$$

The value of K_w is temperature-dependent and it is an equilibrium constant.

$$\begin{aligned} \text{The molarity (M) of pure H}_2\text{O} &= \frac{\text{Density}}{M_w} \\ &= \left(\frac{1000 \text{ g L}^{-1}}{18.0 \text{ g mol}^{-1}} \right) \\ &= 55.55 \text{ M} \end{aligned}$$

Therefore, the ratio of dissociated H_2O to the undissociated H_2O is

$$\frac{10^{-7}}{55.55} = 1.8 \times 10^{-9} \text{ or } \sim 2 \times 10^{-9}.$$

Thus, equilibrium lies mainly towards undissociated water.

Therefore, acidic, neutral, and basic aqueous solutions can

be distinguished by the relative values of the $\text{H}_3\text{O}^{\oplus}$ and OH^{\ominus} concentrations:

$$\text{Acidic: } [\text{H}_3\text{O}^{\oplus}] > [\text{OH}^{\ominus}]$$

$$\text{Neutral: } [\text{H}_3\text{O}^{\oplus}] = [\text{OH}^{\ominus}]$$

$$\text{Basic: } [\text{H}_3\text{O}^{\oplus}] < [\text{OH}^{\ominus}]$$

Temperature ($^{\circ}\text{C}$) \Rightarrow	0	10	20	25	30	40	50
$K_w (\times 10^{-14})$	0.114	0.292	0.681	1.008	1.468	2.919	5.474

8.7 THE pH SCALE

Soren Sorensen (1909) introduced the pH scale to determine the concentration of $\text{H}_3\text{O}^{\oplus}$ in the solution. The pH of a solution is the negative logarithm to the base 10 of the concentration of H^{\oplus} ions which it contains.

Basically 'p' acts as a mathematical operator:

$$\text{p(A)} = -\log_{10}[\text{A}]$$

$$\therefore \text{pH} = -\log_{10}[\text{H}^{\oplus}] \text{ and } \text{pOH} = -\log_{10}[\text{OH}^{\ominus}]$$

At 25°C (298 K), using this definition, a scale called pH scale is developed as follows:

$$\text{For pure H}_2\text{O: } [\text{H}^{\oplus}] = [\text{OH}^{\ominus}] = 10^{-7} \text{ M}$$

$$\text{pH} = -\log_{10}[10^{-7}] = 7 = \text{pOH}$$

$$\text{For pure water at } 25^{\circ}\text{C: } \text{pH} = \text{pOH} = 7.$$

a. If $[\text{H}^{\oplus}] > 10^{-7} \text{ M}$ in a solution, i.e. solution is acidic, then $\text{pH} < 7$.

b. If $[\text{H}^{\oplus}] < 10^{-7} \text{ M}$ in a solution, i.e. solution is basic, then $\text{pH} > 7$.

At 25°C 298 K														
	pH	1	2	3	4	5	6	7	8	9	10	11	12	13
		Acidic solution						H_2O	Basic solution					
		Acidity increases						pH	\longrightarrow					
		\longleftarrow						Neutral	basicity increases					

In general, pH of a solution describes whether it is basic or acidic.

$$\text{For an aqueous solution, } \text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$[K_w = 1 \times 10^{-14} \text{ at } 25^{\circ}\text{C}]$$

As temperature increases, both pH and pOH of pure water decreases since there will be an increase in $[\text{H}^{\oplus}]$ and $[\text{OH}^{\ominus}]$ due to increased dissociation.

A change in pH by just one unit means change in $[\text{H}^{\oplus}]$ by a factor of 10. Similarly, when $[\text{H}^{\oplus}]$ changes by a factor of 100. The value of pH changes by 2 units. That is why the change in pH with temperature is often ignored.

The pH of solution can be found roughly with the help of pH paper that has different colours in solutions of different pH. Now-a-days, pH paper is available with four stripes on it. The different strips have different colours at the same pH. The pH in the range of 1–14 can be determined with an accuracy of ~ 0.5 using pH paper.

For greater accuracy, pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic application.

Table 8.3 The pH of some common substances

Name of the fluid	pH
Concentrated HCl	~ 1.0
1 M HCl solution	~ 0
Gastric juice	~ 1.2
Lemon juice	~ 2.2
Soft drinks and vinegar	~ 3.0
Tomato juice	~ 4.2
Black coffee	5.0
Human Saliva	6.4
Milk	6.8
Human blood	7.4
Egg white, sea water	7.8
Milk of magnesia	10
Lime water	10.5
0.1 M NaOH solution	13
Saturated solution of NaOH	~ 15

8.7.1 ACIDITY AND PH SCALE

Acidic strength means the tendency of an acid to give H_3O^+ or H^+ in water and basic strength means the tendency of a base to give OH^- ions in water. So more the tendency of the substance to give H^+ or OH^- ions, more will be the acidic or basic strength of the substance.

Many properties of aqueous solution depend on the concentration of H_3O^+ or H^+ ions in the solutions and therefore there is a need to express these concentrations in some other simpler terms. For this purpose, Sorenson introduced the concept of pH. pH is the negative logarithm of activity of H^+ ions.

$\therefore \text{pH} = -\log a_{\text{H}^+}$ (where a_{H^+} is the activity of H^+ ions).

Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a solution. By free, we mean those H^+ (or H_3O^+) that are at a large distance from the other H^+ or H_3O^+ ions, so as not to experience its pull. We can infer from this that in dilute solutions, the activity of an ion is same as its concentrations since more number of solvent molecules would separate the two ions. But for concentrated solutions, the activity would be much less than the concentration itself. Therefore, the earlier given expression of pH can be modified for dilute solutions as, $\text{pH} = -\log [\text{H}^+]$. This assumption can only be made when the solution is very much dilute, i.e. $[\text{H}^+] \leq 1 \text{ M}$. For higher concentration of H^+ (or H_3O^+) ions, one needs to calculate the activity experimentally and then calculate the pH.

Thus, for dilute solutions, $\text{pH} = -\log [\text{H}^+] = -\log [\text{H}_3\text{O}^+]$

and $\text{pOH} = -\log [\text{OH}^-]$

For pure water, $\text{pH} = -\log 1 \times 10^{-7} = 7 \log 10 = 7$

Sorenson devised a scale called pH scale for measuring the acidity of a solution. The scale was marked from 0 to 14 with central point at 7. $\text{pH} = 7$ represents a neutral solution, $\text{pH} < 7$ represents an acidic solution and $\text{pH} > 7$ implies alkaline solution. This scale was devised keeping water as solvent at 25°C . If the

temperature and the solvent are changed, the pH range of the scale will also change.

8.7.2 PH OF STRONG ACIDS OR STRONG BASES

- In calculating $[\text{H}_3\text{O}^+]$ in an aqueous solution of strong acid, the strong acid is the only significant source of H_3O^+ unless the solution is extremely dilute (e.g., $< 10^{-6} \text{ M}$) and accordingly pH can be calculated.
- In calculation of $[\text{OH}^-]$ in an aqueous solution of a strong base, the strong base is the only significant source of OH^- unless the solution is extremely dilute $[\text{OH}^-] < 10^{-6} \text{ M}$.
- Total $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ in mixture of strong acids or strong bases.

$$[\text{H}_3\text{O}^+] = \frac{\sum NV}{\sum V}, \quad [\text{OH}^-] = \frac{\sum NV}{\sum V},$$

and pH can be calculated accordingly.

The resultant solution of a mixture of strong acid (normality N_1 and volume V_1) and strong base (normality N_2 and volume V_2)

i. is neutral if $N_1V_1 = N_2V_2$

ii. is basic if $N_2V_2 > N_1V_1$.

$$\therefore [\text{OH}^-]_{\text{resultant}} = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

iii. is acidic if $N_1V_1 > N_2V_2$.

$$\therefore [\text{H}_3\text{O}^+]_{\text{resultant}} = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

8.7.3 LIMITATIONS OF PH SCALE

The pH values of the solutions do not give the exact idea of their relative strengths. For example

- A solution of $\text{pH} = 1$, has $[\text{H}^+]$ 100 times than that of a solution of $\text{pH} = 3$, and not 3 times.
- A $4 \times 10^{-5} \text{ M}$ HCl is twice concentrated as compared to $2 \times 10^{-5} \text{ M}$ HCl solution but the pH values of these solutions are 4.4 and 4.7, respectively, and not double.
- $\text{pH} = 0$ is obtained in 1 N solution of a strong acid, but for concentrations 2 N, 3 N, 10 N, etc, the value can be negative too. Similarly, for a concentrated solution of a strong base ($> 1 \text{ M}$), pH can be greater than 14.
- A 10^{-7} M and 10^{-8} M solution of strong acid can not have $\text{pH} = 7$ and 8, respectively
(See section 8.7.5).

Note: In solving pH of solutions or in calculating the concentration of H^+ or OH^- , the value of logarithm of some commonly used numerals must be remembered.

$$\log 2 = 0.3010 \approx 0.3$$

$$\log 3 = 0.4771 \approx 0.48$$

$$\log 5 = 0.6990 \approx 0.7$$

$$\log 7 = 0.8451 \approx 0.85$$

$$\sqrt{10} = 3.162, \sqrt{2} = 1.414, \sqrt{3} = 1.732, \sqrt{5} = 2.236$$

ILLUSTRATION 8.10

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

Sol. $\text{pH} = -\log [3.8 \times 10^{-3}] = -\log(3.8) - \log(10^{-3})$
 $= -0.58 - (-3) = 2.42$

$$\text{pH} = 2.42 \text{ (solution is acidic)}$$

ILLUSTRATION 8.11

Calculate the pH of the following solutions.

a. 10^{-2} M HCl

b. 10^{-3} M H_2SO_4

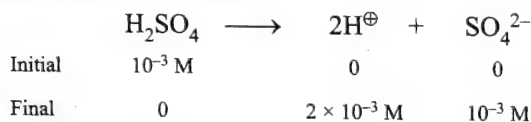
c. 0.2×10^{-2} M NaOH

d. 0.3×10^{-3} M $\text{Ca}(\text{OH})_2$

Sol. Since HCl is monobasic strong acid, and is completely ionised

a. $\text{pH} = -\log(10^{-2}) = 2$

b. Since H_2SO_4 is dibasic strong (n factor = 2). Therefore concentration of H^+ ions = 2×10^{-3} N



$$\text{pH} = -\log(2 \times 10^{-3}) = -\log 2 - \log(10^{-3})$$

$$= -0.3 + 3 = 2.7$$

c. First method:

Since NaOH is monoacidic strong base, so

$$[\text{OH}^-] = 0.2 \times 10^{-2} \text{ M} = 2 \times 10^{-3}$$

So, first calculate pOH of NaOH and then calculate pH accordingly.

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2) - \log(10^{-3})$$

$$= -0.3 + 3 = 2.7$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.7 = 11.3$$

Second method:

First calculate $[\text{H}_3\text{O}^+]$ and then calculate pH accordingly.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\therefore [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{2 \times 10^{-3}}$$

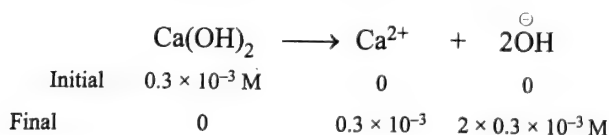
$$= 0.5 \times 10^{-11} = 5 \times 10^{-12}$$

$$\therefore \text{pH} = -\log 5 - \log(10^{-12}) = -0.7 + 12 = 11.3$$

d. Since $\text{Ca}(\text{OH})_2$ is diacidic strong base, thus

$$[\text{OH}^-] = 2 \times 0.3 \times 10^{-3} \text{ N } (n \text{ factor} = 2)$$

or



$$\therefore \text{pOH} = -\log(2 \times 0.3 \times 10^{-3} \text{ N})$$

$$= -\log(6 \times 10^{-4} \text{ N})$$

$$= -\log(3 \times 2) - \log(10^{-4})$$

$$= -\log 3 - \log 2 + 4$$

$$= -0.48 - 0.3 + 4 = 3.22$$

$$\text{Therefore, pH} = 14 - 3.22 = 10.78$$

ILLUSTRATION 8.12

Calculate the concentration of hydrogen ion in the acidic solution with pH.

a. 4.3

b. 5.8239

c. 3.155

Sol.

a. $\text{pH} = -\log [\text{H}_3\text{O}^+]$

$$\therefore \log [\text{H}_3\text{O}^+] = -4.3 = -4 - 0.3 + 1 - 1$$

$$= \bar{5}.7$$

$$\therefore [\text{H}_3\text{O}^+] = \text{Antilog}(\bar{5}.7)$$

$$= 5 \times 10^{-5} \text{ N} = 0.5 \times 10^{-4} \text{ N}$$

b. $\text{pH} = -\log [\text{H}_3\text{O}^+] = 5.8239$

$$\therefore \log [\text{H}_3\text{O}^+] = -5.8239 = -5 - 0.8239 + 1 - 1$$

$$= \bar{6}.1761$$

$$\therefore [\text{H}_3\text{O}^+] = \text{Antilog}(\bar{6}.1761)$$

$$= 1.5 \times 10^{-6} \text{ N}$$

c. $\text{pH} = -\log [\text{H}_3\text{O}^+] = 3.155$

$$\therefore \log [\text{H}_3\text{O}^+] = -3.155 = -3 - 0.155 + 1 - 1$$

$$= \bar{4}.845$$

$$\therefore [\text{H}_3\text{O}^+] = \text{Antilog}(\bar{4}.845)$$

$$= 7 \times 10^{-4} = 0.7 \times 10^{-3} \text{ N}$$

ILLUSTRATION 8.13

Calculate the concentration of OH^- in the solution of base with pH.

a. 10.4771

b. 12.301

c. 11.8451

Sol. Since the solutions are basic, so first calculate pOH of the

solution and then calculate $[\text{OH}^-]$ accordingly.

a. $\text{pH} = 10.4771$

$$\text{pOH} = 14 - 10.4771 = 3.5229$$

$$\text{pOH} = -\log [\text{OH}^-] = 3.5229$$

$$\therefore \log [\text{OH}^-] = -3.5229 = -3 - 0.5229 + 1 - 1$$

$$= \bar{4}.4771$$

$$\therefore [\text{OH}^-] = \text{Antilog}(\bar{4}.4771)$$

$$= 3 \times 10^{-4} = 0.3 \times 10^{-3} \text{ N}$$

c. $\text{pH} = 12.301$

$$\text{pOH} = 14 - 12.301 = 1.699$$

$$\text{pOH} = -\log [\text{OH}^-] = 1.699$$

$$\therefore \log [\text{OH}^-] = -1.699 = -1 - 0.699 + 1 - 1$$

$$= \bar{2}.301$$

$$\therefore [\text{OH}^-] = \text{Antilog}(2.301) \\ = 2 \times 10^{-2} \text{ N} = 0.2 \times 10^{-1} \text{ N}$$

$$\text{pH} = 11.8451 \\ \text{pOH} = 14 - 11.8451 = 2.1549$$

$$\text{pOH} = -\log[\text{OH}^-] = 2.1549$$

$$\therefore \log[\text{OH}^-] = -2.1549 = -2 - 0.1549 + 1 - 1 \\ = \bar{3}.8451$$

$$\therefore [\text{OH}^-] = \text{Antilog}(\bar{3}.8451) \\ = 7 \times 10^{-3} \text{ N} = 0.7 \times 10^{-2} \text{ N}$$

ILLUSTRATION 8.14

Calculate the pH of the following mixtures of strong acids, strong bases, and combination of both.

- 500 mL of 0.1 M HCl + 200 mL of 0.1 M H_2SO_4 + 300 mL of 0.2 M HNO_3 .
- 100 mL of 0.1 M HCl + 100 mL of 0.2 M H_2SO_4 + 100 mL of 0.1 M HNO_3 and 700 mL of H_2O .
- 500 mL of 0.1 M NaOH + 100 mL of 0.1 M $\text{Ca}(\text{OH})_2$ + 400 mL of 0.2 M KOH.
- 100 mL of 0.1 M NaOH + 200 mL of 0.1 N $\text{Ca}(\text{OH})_2$ + 200 mL of 0.1 M KOH and 500 mL of H_2O .
- 100 mL of 0.1 M HCl + 300 mL of 0.1 M H_2SO_4 + 100 mL of 0.3 M $\text{Ba}(\text{OH})_2$ and volume was made to 1 L by adding water.
- 500 mL of 0.1 M HCl + 100 mL of 0.1 N H_2SO_4 + 400 mL of 0.1 M $\text{Ca}(\text{OH})_2$.
- 8 g of NaOH + 680 mL of 1 M HCl + 10 mL of H_2SO_4 (specific gravity 1.2, 49% H_2SO_4 by mass). The total volume of the solution was made to 1 L with water.
- 37.0 g of $\text{Ca}(\text{OH})_2$ + 360 mL of 1 M HCl + 10 mL of H_2SO_4 (density = 1.4, 49% H_2SO_4 by mass). The total volume of the solution was made to 1 L with water.

Sol.

- a. All are strong acid and completely ionised.

$$\text{Total volume} = 500 + 200 + 300 = 1000 \text{ mL}$$

$$N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$$

$$N_4 = \frac{N_1V_1 + N_2V_2 + N_3V_3}{(V_1 + V_2 + V_3)}$$

$$(V_4 = V_1 + V_2 + V_3 = 1000 \text{ mL})$$

$$\frac{0.1 \times 1 \times 500 + 0.1 \times 2 \times 200 + 0.2 \times 1 \times 300}{1000}$$

$$= \frac{50 + 40 + 60}{1000} = \frac{150}{1000} = 15 \times 10^{-2} \text{ N}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log(15 \times 10^{-2})$$

$$= -\log(5 \times 3) - \log(10^{-2})$$

$$= -0.7 - 0.48 + 2 = 0.82$$

$$\text{b. Total volume} = 100 + 100 + 100 + 700 \text{ mL } \text{H}_2\text{O} \\ = 1000 \text{ mL}$$

$$100 \times 0.1 \times 1 + 100 \times 0.2 \times 2 \text{ (n factor)} \\ + 100 \times 0.1 \times 1$$

$$N_4 = \frac{1000}{1000}$$

$$= \frac{10 + 40 + 10}{1000} = \frac{60}{1000} = 6 \times 10^{-2} \text{ N}$$

$$\therefore \text{pH} = -\log(6 \times 10^{-2}) = -\log(3 \times 2) - \log 10^{-2} \\ = -\log 3 - \log 2 + 2 \\ = -0.48 - 0.3 + 2 = 1.22$$

- c. All are strong bases and completely ionised.

Thus first calculate $[\text{OH}^-]$ and pOH then calculate pH accordingly

$$500 \times 0.1 \times 1 + 100 \times 0.1 \times 2 \text{ (n factor)} \\ + 400 \times 0.2 \times 1$$

$$N_4 = \frac{500 + 100 + 400}{1000}$$

$$= \frac{50 + 20 + 80}{1000} = \frac{150}{1000} = 15 \times 10^{-2} \text{ N}$$

$$\therefore \text{pOH} = -\log[\text{OH}^-] = -\log(15 \times 10^{-2}) \\ = -\log(5 \times 3) - \log 10^{-2} \\ = -\log 5 - \log 3 + 2 \\ = -0.7 - 0.48 + 2 \\ = 0.82$$

$$\therefore \text{pH} = 14 - 0.82 = 13.18$$

- d. Note: Solution of $\text{Ca}(\text{OH})_2$ is given in normality so need not to be multiplied by 'n factor'

$$N_4 = \frac{100 \times 0.1 \times 1 + 200 \times 0.1 \times 1 + 200 \times 0.1 \times 1}{100 + 200 + 200 + 500 \text{ mL of } \text{H}_2\text{O}}$$

$$= \frac{10 + 20 + 20}{1000} = \frac{50}{1000} = 5 \times 10^{-2} \text{ N}$$

$$\therefore \text{pOH} = -\log[\text{OH}^-] = -\log(5 \times 10^{-2}) \\ = -\log 5 - \log 10^{-2} \\ = -0.7 + 2 = 1.3$$

$$\therefore \text{pH} = 14 - 1.3 = 12.7$$

- e. Here, mixture of strong acid and strong bases is given. So first calculate the mEq of acids and bases.

- i. If the mEq of strong acid is in excess, then calculate the pH from the concentration of $[\text{H}^+]$ left.

- ii. If the mEq of strong bases is in excess, then calculate the pOH from the concentration of $[\text{OH}^-]$ left and then calculate pH accordingly.

Total mEq of strong acids

$$= 100 \times 0.1 \times 1 + 300 \times 0.1 \times 2 \text{ (n factor)} \\ = 10 + 60 = 70 \text{ mEq}$$

$$\text{Total mEq strong base} = 100 \times 0.3 \times 2 \text{ (n factor)} \\ = 60 \text{ mEq}$$

mEq of strong acid left = $70 - 60 = 10$ mEq

Total volume of solution = $1 \text{ L} = 1000 \text{ mL}$

$$\therefore [\text{H}^+] = \frac{10}{1000} = 10^{-2} \text{ N}$$

$$\text{pH} = -\log(10^{-2}) = 2$$

f. Proceed as in part (e).

(Here H_2SO_4 is given in normality)

Total mEq of strong acid = $500 \times 0.1 \times 1 + 100 \times 0.1 \times 1$

$$= 50 + 10 = 60 \text{ mEq}$$

Total mEq of strong base = $400 \times 0.1 \times 2$ (n factor)

$$= 80 \text{ mEq}$$

mEq of strong base left = $80 - 60 = 20$ mEq

Total volume of solution = $500 + 100 + 400$

$$= 1000 \text{ mL}$$

$$\therefore [\text{OH}^-] = \frac{20}{1000} = 2 \times 10^{-2} \text{ N}$$

$$\begin{aligned} \therefore \text{pOH} &= -\log(2 \times 10^{-2}) \\ &= -\log 2 - \log 10^{-2} \\ &= -0.3 + 2 = 1.7 \end{aligned}$$

$$\text{Thus, pH} = 14 - 1.7 = 12.3.$$

g. Moles of NaOH = $\frac{8}{40}$ (M_w of NaOH = 40)

$$= 0.2 \text{ mol} = 200 \text{ mmol}$$

$$N_{\text{H}_2\text{SO}_4} = \frac{\% \text{ by weight} \times 10 \times d}{Ew_2}$$

$$= \frac{49 \times 10 \times 1.2}{49} = 12 \text{ N}$$

mEq of H_2SO_4 = $12 \text{ N} \times 10 \text{ mL} = 120 \text{ mEq}$

mEq of HCl = $680 \times 1 \times 1 = 680 \text{ mEq}$

Total mEq of acid = $120 + 680 = 800 \text{ mEq}$

mEq of acid left = $800 - 200 = 600 \text{ mEq}$

Total volume = 1000 mL

$$\therefore [\text{H}^+] = \frac{600}{1000} = 6 \times 10^{-1} \text{ N}$$

$$\begin{aligned} \text{pH} &= -\log(6 \times 10^{-1}) = -\log(3 \times 2) - \log 10^{-1} \\ &= -\log 3 - \log 2 + 1 \\ &= -0.48 - 0.3 + 1 = 0.22 \end{aligned}$$

h. M_w of $\text{Ca}(\text{OH})_2 = 74$

$$Ew \text{ of } \text{Ca}(\text{OH})_2 = \frac{74}{2} = 37 \text{ g Eq}^{-1}$$

$$\text{Eq of } \text{Ca}(\text{OH})_2 = \frac{37}{37} = 1 \text{ Eq} = 1000 \text{ mEq}$$

$$N_{\text{H}_2\text{SO}_4} = \frac{\% \text{ by weight} \times 10 \times d}{Ew_2} = \frac{49 \times 10 \times 1.4}{49}$$

$$= 14 \text{ N}$$

mEq of H_2SO_4 = $14 \text{ N} \times 10 \text{ mL} = 140 \text{ mEq}$

mEq of HCl = $360 \text{ mL} \times 1 \text{ N} = 360 \text{ mEq}$

Total mEq of acid = $(140 + 360) = 500 \text{ mEq}$

mEq of base left = $1000 - 500 = 500 \text{ mEq}$

Total volume = 1000 mL

$$\therefore [\text{OH}^-] = \frac{500}{1000} = 0.5 \text{ N} = 5 \times 10^{-1} \text{ N}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$= -\log(5 \times 10^{-1})$$

$$= -\log 5 - \log 10^{-1} = -0.7 + 1 = 0.3$$

$$\text{Thus, pH} = 14 - 0.3 = 13.7$$

8.7.4 CALCULATION OF THE AMOUNT OF STRONG ACID OR STRONG BASE (WHEN THE PH OF A SOLUTION IS GIVEN)

If the pH of the solution is in acidic range (< 7) then the concentration of H^+ in normality is calculated.

$$\text{Strength (g L}^{-1}\text{)} = N \times Ew \text{ or } M \times Mw$$

(Ew = Equivalent weight, Mw = Molecular weight)

If the pH of solution is in basic range (> 7), pOH and then

the concentration of OH^- in normality, is calculated. Then again

$$\text{Strength (g L}^{-1}\text{)} = N \times Ew \text{ or } M \times Mw$$

For example:

i. pH of HCl is 4.7. The amount of HCl in 1 L of solution is

$$\text{pH} = -\log [\text{H}^+] = 4.7$$

$$\log [\text{H}^+] = -4.7 = -4 - 0.7 + 1 - 1 = \bar{5}.3$$

$$\therefore [\text{H}^+] = \text{Antilog}(\bar{5}.3) = 2 \times 10^{-5} \text{ N}$$

$$\text{Strength of HCl} = 2 \times 10^{-5} \times 36.5$$

$$(Mw = Ew \text{ of HCl} = 36.5)$$

$$= 73 \times 10^{-5} \text{ g L}^{-1}.$$

ii. pH of NaOH is 10.48. The amount of NaOH per litre solution is:

$$\text{pH} = 10.48$$

$$\text{pOH} = 14 - 10.48 = 3.52$$

$$-\log [\text{OH}^-] = 3.52$$

$$\log [\text{OH}^-] = -3.52 = -3 - 0.52 + 1 - 1 = \bar{4}.48$$

$$[\text{OH}^-] = \text{Antilog}(\bar{4}.48) = 3 \times 10^{-4} \text{ N.}$$

$$\text{Strength of NaOH} = 3 \times 10^{-4} \times 40$$

$$(Mw = Ew \text{ of NaOH} = 40)$$

$$= 120 \times 10^{-4} = 1.2 \times 10^{-2} \text{ g L}^{-1}$$

ILLUSTRATION 8.15

- What amount of H_2SO_4 must be dissolved in 500 mL of solution to have a pH of 2.15?
- What amount of KOH must be dissolved in 200 mL of solution to have a pH of 12.3?
- What amount of $\text{Ca}(\text{OH})_2$ must be dissolved in 100 mL of solution to have a pH of 13.85?

Sol.

a. pH = 2.15

$$-\log [\text{H}^+] = 2.15$$

$$\log [\text{H}^+] = -2.15 = -2 - 0.15 + 1 - 1 = \bar{3}.85$$

$$[\text{H}^+] = \text{Antilog}(\bar{3}.85) = 7 \times 10^{-3} \text{ N}$$

$$\text{Strength of H}_2\text{SO}_4 (\text{g L}^{-1}) = N \times E_w$$

$$\left(E_w \text{ of H}_2\text{SO}_4 = \frac{98}{2} = 49 \right)$$

$$= 7 \times 10^{-3} \times 49 = 0.343 \text{ g L}^{-1}$$

$$= \frac{0.343 \times 500 \text{ mL}}{1000 \text{ mL}} = 0.1715 \text{ g/500 mL}$$

Alternatively:

$$\text{Strength of H}_2\text{SO}_4 (\text{g L}^{-1})$$

$$= M \times Mw$$

$$\left(M = \frac{7 \times 10^{-3} \text{ N}}{2} \right)$$

$$= \frac{7 \times 10^{-3}}{2} \times 98 = 7 \times 10^{-3} \times 49 \text{ g L}^{-1}$$

$$= \frac{7 \times 10^{-3}}{2} \text{ g/500 mL} = 0.1715 \text{ g/500 mL}$$

- b. Since $\text{pH} \gg 7$ (basic solution), first calculate pOH and $[\text{OH}^-]$. Then calculate amount of $\text{KOH}/200 \text{ mL}$
 $\text{pH} = 12.3$, $\text{pOH} = 14 - 12.3 = 1.7$

$$-\log [\text{OH}^-] = 1.7$$

$$\log [\text{OH}^-] = -1.7 = -1 - 0.7 + 1 - 1 = \bar{2}.3$$

$$[\text{OH}^-] = \text{Antilog}(\bar{2}.3) = 2 \times 10^{-2} \text{ N.}$$

$$\text{Strength of KOH (g L}^{-1}\text{)}$$

$$= N \times E_w \text{ or } M \times Mw \quad (Mw = E_w \text{ of KOH} = 56 \text{ g})$$

$$= 2 \times 10^{-2} \times 56 \text{ g L}^{-1}$$

$$= \frac{2 \times 10^{-2} \times 56 \times 200 \text{ mL}}{1000 \text{ mL}} \text{ g/200 mL}$$

$$= 0.224 \text{ g/200 mL}$$

- c. $[Mw \text{ of Ca(OH)}_2 = 74 \text{ g, } E_w \text{ of Ca(OH)}_2 = \frac{74}{2} = 37 \text{ g}]$
 $\text{pH} = 13.85$, $\text{pOH} = 14 - 13.85 = 0.15$

$$\log [\text{OH}^-] = -0.15 + 1 - 1 = \bar{1}.85$$

$$[\text{OH}^-] = \text{Antilog}(\bar{1}.85) = 7 \times 10^{-1} \text{ N or } \frac{7 \times 10^{-1}}{2} \text{ M}$$

$$\text{Strength (g L}^{-1}\text{)} = (7 \times 10^{-1} \text{ N} \times 37) \text{ g L}^{-1}$$

$$\text{or } \left(\frac{7 \times 10^{-1}}{2} \times 74 \right) \text{ g L}^{-1}$$

$$= \frac{7 \times 10^{-1} \times 37 \times 100 \text{ mL}}{1000 \text{ mL}} \text{ g/100 mL}$$

$$= 2.59 \text{ g/100 mL}$$

Thus, calculate the total concentration of $[\text{H}^+]$ or $[\text{OH}^-]$ and then divide by 2.

Case II: When equal volumes of three solutions with known pH are given, the volume becomes three times and concentration final

$[\text{H}^+]$ or $[\text{OH}^-]$ becomes $1/3$. Thus, calculate the total concentration of $[\text{H}^+]$ or $[\text{OH}^-]$ and then divide by 3.

Example:

Case I: Equal volumes of two solution with $\text{pH} = 2$ and $\text{pH} = 3$ are mixed. The final pH of solution is

$$\text{pH} = 2, \therefore [\text{H}^+] = 10^{-2} \text{ N}$$

$$\text{pH} = 3, \therefore [\text{H}^+] = 10^{-3} \text{ N}$$

$$\text{Final } [\text{H}^+] = \frac{(10^{-2} + 10^{-3})}{2}$$

$$= \frac{10^{-2}}{2} (1 + 10^{-1}) = \frac{1.1}{2} \times 10^{-2}$$

$$= 0.55 \times 10^{-2} = 55 \times 10^{-4}$$

$$\therefore \text{pH of final solution} = -\log (55 \times 10^{-4})$$

$$= -\log 55 - \log 10^{-4}$$

$$= -1.74 + 4 = 2.26$$

Alternative approximation method:

When the difference in two pH is one. Take the average pH and subtract 0.24 to get the exact final pH.

$$\text{Approximate final pH} = \frac{2 + 3}{2} = 2.5$$

$$\text{Actual pH final} = 2.5 - 0.24 = 2.26$$

If the two pH are 3 and 4. The final pH is:

$$\text{Approximate final pH} = \frac{3 + 4}{2} = 3.5$$

$$\text{Actual final pH} = 3.5 - 0.24 = 3.26$$

Checking of actual pH:

$$\text{Final } [\text{H}^+] = \left(\frac{10^{-3} + 10^{-4}}{2} \right) = \frac{10^{-3}}{2} (1 + 10^{-1})$$

$$= 0.55 \times 10^{-3} = 55 \times 10^{-5}$$

$$\text{Final pH} = -\log (55 \times 10^{-5})$$

$$= -\log 55 - \log 10^{-5}$$

$$= -1.74 + 5 = 3.26$$

Case II: Equal volumes of three solutions with $\text{pH} = 1, 2$, and 3 are mixed. The final pH of solution is

$$\text{pH} = 1, [\text{H}^+] = 10^{-1} \text{ N,}$$

$$\text{pH} = 2, [\text{H}^+] = 10^{-2} \text{ N}$$

$$\text{pH} = 3, [\text{H}^+] = 10^{-3} \text{ N}$$

$$\text{Final } [\text{H}^+] = \frac{(10^{-1} + 10^{-2} + 10^{-3})}{3}$$

$$= \frac{10^{-1}}{3} (1 + 0.1 + 0.01)$$

(neglect 0.01)

$$= \frac{1.1}{3} \times 10^{-1}$$

$$= 0.366 \times 10^{-1} \text{ N} = 366 \times 10^{-4} \text{ N}$$

8.7.5 CALCULATION OF pH AND CONCENTRATION OF $[\text{H}^+]$ OR $[\text{OH}^-]$ (WHEN EQUAL VOLUMES OF TWO OR THREE SOLUTIONS OF KNOWN pH ARE MIXED)

Case I: When equal volumes of two solutions with known pH are given, the final volume becomes double and concentration of

$[\text{H}^+]$ or $[\text{OH}^-]$ is halved.

$$\begin{aligned}\therefore \text{pH of final solution} &= -\log(366 \times 10^{-4}) \\ &= -\log 366 - \log 10^{-4} \\ &= -2.5635 + 4 = 1.4365 \approx 1.44\end{aligned}$$

Alternative approximation method:

When the three pH differ by one unit, take the average pH and subtract 0.56 to get final exact pH.

$$\text{Approximate final pH} = \frac{1+2+3}{3} = 2.$$

$$\text{Actual final pH} = 2.0 - 0.56 = 1.44$$

If three pH are 2, 3, and 4. Then final pH is

$$\text{Approximate final pH} = \frac{2+3+4}{3} = 3$$

$$\text{Actual final pH} = 3.0 - 0.56 = 2.44$$

Checking of actual pH:

$$\begin{aligned}\text{Final } [H^{\oplus}] &= \frac{(10^{-2} + 10^{-3} + 10^{-4})}{3} \\ &= \frac{10^{-2}}{3} (1 + 0.1 + 0.01) \quad (\text{neglect } 0.01) \\ &= \frac{1.1}{3} \times 10^{-2} = 0.366 \times 10^{-2} = 366 \times 10^{-5}\end{aligned}$$

$$\begin{aligned}\text{Final pH} &= -\log(366 \times 10^{-5}) \\ &= -2.5635 + 5 = 2.4365 \approx 2.44\end{aligned}$$

ILLUSTRATION 8.16

Calculate the pH of solution made by mixing equal volumes of:

- Two solutions having pH = 1.5 and 2.5.
- Three solutions having pH = 1.5, 2.5, and 3.5.
- Two solutions having pH = 8 and 9.
- Three solutions having pH = 8, 9, and 10.
- Two solutions having pH = 2 and 4.
- Three solutions having pH = 2, 4, and 6.

Sol.

- a. The two pH values differ by one unit.

$$\text{Approximate final pH} = \frac{(1.5 + 2.5)}{2} = 2$$

$$\text{Actual final pH} = 2.0 - 0.24 = 1.76$$

Checking final pH:

$$\text{pH} = 1.5, \quad \log [H^{\oplus}] = -1.5 = -1 - 0.5 + 1 - 1 = \bar{2}.5$$

$$[H^{\oplus}] = \text{Antilog}(\bar{2}.5) \approx 3 \times 10^{-2} \text{ N}$$

$$\text{pH} = 2.5, \quad \log [H^{\oplus}] = -2.5 = -2 - 0.5 + 1 - 1 = \bar{3}.5$$

$$[H^{\oplus}] = \text{Antilog}(\bar{3}.5) \approx 3 \times 10^{-3} \text{ N.}$$

$$\begin{aligned}\text{Final } [H^{\oplus}] &= \frac{(3 \times 10^{-2} + 3 \times 10^{-3})}{2} \\ &= \frac{3 \times 10^{-2}}{2} [1 + 0.1] \\ &= \frac{1.1}{2} \times 3 \times 10^{-2}\end{aligned}$$

$$\begin{aligned}&= 0.55 \times 3 \times 10^{-2} = 55 \times 3 = 10^{-4} \\ \text{pH} &= -\log(55) - \log 3 - \log 10^{-4} \\ &= -1.74 - 0.5 + 4 \quad (\text{taking } \log 3 \approx 0.48 \approx 0.5) \\ &= -2.24 + 4 = 1.76\end{aligned}$$

- b. The three pH values differ by one unit

$$\text{Approximate final pH} = \frac{(1.5 + 2.5 + 3.5)}{3} = \frac{7.5}{3} = 2.5$$

$$\text{Actual final pH} = 2.5 - 0.56 = 1.94$$

Checking final pH:

Proceed as above in part (a).

$$\text{pH} = 1.5, \therefore [H^{\oplus}] \approx 3 \times 10^{-2} \text{ N}$$

$$\text{pH} = 2.5, \therefore [H^{\oplus}] \approx 3 \times 10^{-3} \text{ N}$$

$$\text{pH} = 3.5, \therefore [H^{\oplus}] \approx 3 \times 10^{-4} \text{ N}$$

$$\begin{aligned}\text{Final } [H^{\oplus}] &= \frac{3 \times (10^{-2} + 10^{-3} + 10^{-4})}{3} \\ &= \frac{3 \times 10^{-2} (1 + 0.1 + 0.01) \text{ (neglect } 0.01)}}{3} \\ &= \frac{1.1 \times 3}{3} \times 10^{-2} \\ &= 0.366 \times 3 \times 10^{-2} = 366 \times 3 \times 10^{-5}.\end{aligned}$$

$$\begin{aligned}\text{pH} &= -\log(366) - \log 3 - \log 10^{-5} \\ &= -2.5635 - 0.5 + 5 \quad (\text{taking } \log 3 = 0.48 \approx 0.5) \\ &= -3.0635 + 5 = 1.9365 \approx 1.94\end{aligned}$$

$$\text{pH} = 1.94$$

- c. Although the pH values are in basic range, so pH of mixture can be calculated as when pH values are in acidic range.

$$\text{Approximate final pH} = \frac{(8 + 9)}{2} = 8.5$$

$$\text{Actual final pH} = 8.5 - 0.24 = 8.26$$

Checking final pH:

$$\text{pH} = 8, \therefore [H^{\oplus}] = 10^{-8} \text{ N}$$

$$\text{pH} = 9, \therefore [H^{\oplus}] = 10^{-9} \text{ N}$$

$$\begin{aligned}\text{Final } [H^{\oplus}] &= \frac{(10^{-8} + 10^{-9})}{2} \\ &= \frac{10^{-8} (1 + 0.1)}{2} \\ &= \frac{1.1}{2} \times 10^{-8} \text{ N} \\ &= 0.55 \times 10^{-8} = 55 \times 10^{-10} \text{ N}\end{aligned}$$

$$\text{pH} = -\log(55) - \log 10^{-10} = -1.74 + 10 = 8.26.$$

- d. Proceed as in part (c).

$$\text{Approximate final pH} = \frac{(8 + 9 + 10)}{3} = 9$$

$$\text{Actual final pH} = 9.0 - 0.56 = 8.44$$

Checking final pH:

$$\begin{aligned}\text{Final } [\text{H}^{\oplus}] &= \frac{(10^{-8} + 10^{-9} + 10^{-10})}{3} \\ &= \frac{10^{-8} (1 + 0.1 + 0.01)}{3} \quad (\text{neglect } 0.01) \\ &= \frac{1.1}{3} \times 10^{-8} = 0.366 \times 10^{-8} = 366 \times 10^{-11}\end{aligned}$$

$$\begin{aligned}\text{pH} &= -\log(366) - \log 10^{-11} \\ &= -2.5635 + 11 = 8.4365 \approx 8.44\end{aligned}$$

- e. The two pH values do not differ by one unit, so calculate the pH directly

$$\begin{aligned}[\text{H}^{\oplus}]_{\text{total}} &= \left(\frac{10^{-2} + 10^{-4}}{2} \right) = \frac{10^{-2}}{2} (1 + 10^{-2}) \\ &\quad (\text{neglect } 10^{-2}) \\ &\approx \frac{10^{-2}}{2} \approx 0.5 \times 10^{-2} \\ &\approx 5 \times 10^{-3} \text{ M}\end{aligned}$$

$$\text{pH} \approx -\log(5 \times 10^{-3}) \approx -0.7 + 3 \approx 2.3$$

- f. Here also, the three pH value do not differ by one unit, so calculate the pH directly.

$$\begin{aligned}[\text{H}^{\oplus}]_{\text{total}} &= \left(\frac{10^{-2} + 10^{-4} + 10^{-6}}{3} \right) = \frac{10^{-2}}{3} (1 + 10^{-2} + 10^{-4}) \\ &\quad (\text{neglect } 10^{-2} \text{ and } 10^{-4}) \\ &\approx \frac{10^{-2}}{3}\end{aligned}$$

$$\text{pH} = -\log \left[\frac{10^{-2}}{3} \right]$$

$$\begin{aligned}\text{pH} &= -\log 10^{-2} + \log 3 \\ &= 2 + 0.48\end{aligned}$$

$$\text{pH} = 2.48$$

8.7.6 CALCULATION OF PH OF EXTREMELY DILUTE ($<10^{-6}$ M) SOLUTION OF STRONG ACIDS AND STRONG BASES

The pH calculation of 10^{-7} M or 10^{-8} M HCl is not correct, since pH of 10^{-7} M and 10^{-8} M HCl will be 7 and 8, respectively. But any acid solution cannot behave neutral (pH = 7) and basic (pH = 8).

Since the $[\text{H}^{\oplus}]$ in any acid solution would always be more than the $[\text{H}^{\oplus}]$ in water alone, therefore, the pH of such dilute solutions are calculated as follows:

Method I

The concentration of H^{\oplus} or $\text{H}_3\text{O}^{\oplus}$ ions from pure water is 10^{-7} M. So add the H^{\oplus} ion concentration from water and H^{\oplus} (or $\text{H}_3\text{O}^{\oplus}$) ion concentration from HCl to get the $[\text{H}^{\oplus}]_{\text{total}}$.

$$\begin{aligned}\therefore [\text{H}^{\oplus}]_{\text{total}} &= [\text{H}^{\oplus}]_{\text{HCl}} + [\text{H}^{\oplus}]_{\text{water}} \\ &= 10^{-7} \text{ M} + 10^{-7} \text{ M} \\ &= 2 \times 10^{-7} \text{ M}\end{aligned}$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^{\oplus}]_{\text{total}} \\ &= -\log(2 \times 10^{-7})\end{aligned}$$

$$\begin{aligned}&= -\log 2 - \log 10^{-7} \\ &= -0.3011 + 7 = 6.6989\end{aligned}$$

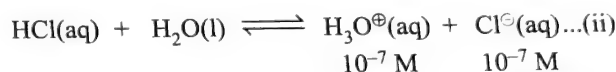
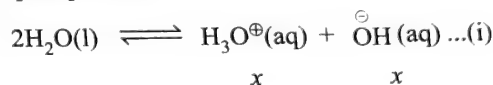
Though the method appears to be correct but there is a mistake in it. According to Le Chatelier's principle, which states that when concentration of a reactant or product is changed, the reaction tends to go forward or reverse to finally establish equilibrium.

In this case, by adding 10^{-7} M HCl to water, the concentration of $[\text{H}^{\oplus}]$ increases, which makes the reaction to go in the reverse direction. Therefore, the $[\text{H}^{\oplus}]$ from water would become less than 10^{-7} M. So, this method gives incorrect result.

Method II

The statement given above that *the addition of an ion to an equilibrium having the same ion makes the equilibrium move in a direction to consume the ion* is called the *common ion effect*. This implies that water would dissociate less in the presence of HCl. Alternatively, due to the common ion (H^{\oplus}) or ($\text{H}_3\text{O}^{\oplus}$), the suppression of ionisation of H_2O takes place in presence of HCl.

$$\text{Let } [\text{H}_3\text{O}^{\oplus}] = [\text{OH}^{\ominus}] = x \text{ M}$$



$$[\text{H}_3\text{O}^{\oplus}]_{\text{Total}} \text{ from equations (i) and (ii)} = (x + 10^{-7}) \text{ M}$$

At equilibrium

$$[\text{H}_3\text{O}^{\oplus}] [\text{OH}^{\ominus}] = 10^{-14} = K_w$$

$$(x + 10^{-7})(x) = 10^{-14}$$

$$\text{or } x^2 + 10^{-7}x - 10^{-14} = 0$$

(This a quadratic equation in x and can be solved by usual

methods. In the solution, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$\therefore x = \frac{-10^{-7} + \sqrt{(10^{-7})^2 + (4 \times 10^{-14})}}{2}$$

$$[\text{OH}^{\ominus}] = x = 0.618 \times 10^{-7} \text{ M}$$

$$\text{Therefore, } [\text{H}_3\text{O}^{\oplus}]_{\text{Total}} = (10^{-7} + 0.618 \times 10^{-7}) \text{ M}$$

$$\therefore \text{pH} = -\log(1.618 \times 10^{-7}) = 6.7910$$

Thus, it is concluded that $[\text{H}_3\text{O}^{\oplus}]$ from water is considered only if $[\text{H}_3\text{O}^{\oplus}]$ from acid is $<10^{-6}$ M and if $[\text{H}_3\text{O}^{\oplus}]$ from acid $\geq 10^{-6}$ M, $[\text{H}_3\text{O}^{\oplus}]$ from water is ignored.

ILLUSTRATION 8.17

While calculating the pH of 10^{-7} M HCl, the common ion effect of HCl on water is considered. Why the common ion effect of water on HCl is not considered?

Sol.

- a. Let the K_w of $\text{H}_2\text{O} = 10^{-10}$ at 25°C . Then in pure water

$$[\text{H}_3\text{O}^{\oplus}] = [\text{OH}^{\ominus}] = 10^{-5} = x.$$

Thus, $[\text{H}_3\text{O}^+]$ from water in the presence of 10^{-7} M HCl using the same value of K_w is:

$$(x + 10^{-7})x = 10^{-10}$$

$$\therefore x = 0.995 \times 10^{-5} \text{ M}$$

The percentage decrease in the concentration of H_3O^+ of water is:

$$\frac{(10^{-5} - 0.995 \times 10^{-5})}{10^{-5}} \times 100 = 0.5\%$$

- b. When the K_w of water was 10^{-14} , the H_3O^+ concentration of pure water was 10^{-7} M while that in the presence of 10^{-7} M HCl was 0.618×10^{-7} M (refer section 8.7.6, method II).

Therefore, the percentage decrease in the concentration of H_3O^+ of water in the presence of 10^{-7} M HCl is:

$$\frac{(10^{-7} - 0.618 \times 10^{-7})}{10^{-7}} \times 100 = 38.2\%$$

Thus, it can be concluded that the larger the value of equilibrium constant of the weak electrolyte, the lesser is the common ion effect produced. So, the common ion effect is experienced more by the weak electrolyte (having smaller equilibrium constant) than the strong electrolyte (having larger equilibrium constant).

ILLUSTRATION 8.18

What is the pH of the following solutions?

- 10^{-8} M HCl
- 5×10^{-8} M HCl
- 5×10^{-10} M HCl
- 10^2 M HCl

Sol.

- a. **pH of 10^{-8} M HCl**

First method:

$$[\text{H}_3\text{O}^+] = 10^{-8} \text{ (from HCl)} + 10^{-7} \text{ (from H}_2\text{O)} \\ = 10^{-7} (10^{-1} + 1) = 1.1 \times 10^{-7}$$

$$\text{pH} = -\log(1.1 \times 10^{-7})$$

$$= -\log 1.1 - \log 10^{-7}$$

$$= -0.0414 + 7 = 6.9586 \approx 6.96$$

Second method:

Since the $[\text{H}_2\text{O}] > [\text{HCl}]$, so suppression of ionisation of H_2O occurs.

$$\text{Let } x = [\text{OH}^-] = [\text{H}_3\text{O}^+] \text{ from H}_2\text{O}.$$

The $[\text{H}_3\text{O}^+]_{\text{total}}$ is generated from the ionisation of HCl dissolved and from ionisation of H_2O .

$$\therefore K_w = (10^{-8} + x)(x) = 10^{-14}$$

$$\text{or } x^2 + 10^{-8}x - 10^{-14} = 0$$

$$\therefore x = \frac{-10^{-8} + \sqrt{(10^{-8})^2 + (4 \times 10^{-14})}}{2}$$

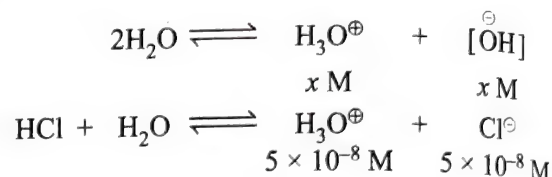
$$[\text{OH}^-] = x = 9.5 \times 10^{-8} \text{ M}$$

$$\text{So, pOH} = 7.02 \text{ and pH} = 6.98$$

- b. **pH of 5×10^{-8} M HCl:**

If the contribution of $[\text{H}_3\text{O}^+]$ from HCl is considered, i.e., $[\text{H}_3\text{O}^+] = 5 \times 10^{-8}$ M. Then pH would be > 7 . This is not possible because $[\text{H}_3\text{O}^+]$ of any acid solution, no matter how dilute it is, cannot be less than that of pure water alone. In such cases, the concentration of $[\text{H}_3\text{O}^+]$ made by water has to be taken.

Let $[\text{H}_3\text{O}^+]$ from water be x M in the presence of 5×10^{-8} M HCl.



At equilibrium, $[\text{H}_3\text{O}^+] = (x + 5 \times 10^{-8})$, $[\text{OH}^-] = x$.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x + 5 \times 10^{-8})(x) = 10^{-14}$$

$$x = 0.78 \times 10^{-7} \text{ M}$$

$$\therefore [\text{H}_3\text{O}^+] = (5 \times 10^{-8} + 0.78 \times 10^{-7}) \\ = 1.28 \times 10^{-7}$$

$$\text{pH} = -\log(1.28 \times 10^{-7}) = -(0.11 - 7) = 6.89$$

- c. **pH of 5×10^{-10} M HCl:**

HCl is so dilute that its contribution to $[\text{H}_3\text{O}^+]$ is negligible as compared with the ionisation of water.

Thus, $[\text{H}^+] = 10^{-7}$ and therefore, $\text{pH} = 7.00$

- d. **pH of 10^2 M HCl:**

	$\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$		
Initial concentration	10^2	0	0
Concentration after dissociation	0	10^2	10^2

$$\text{pH} = -\log(10^2) = -2$$

A negative pH only means that the $[\text{H}^+] > 1 \text{ M}$.

However, in actual practice, a negative pH is uncommon. Firstly, even strong acids (say 100% H_2SO_4) become partially dissociated at high concentration.

According to Sorenson, pH is related to thermo-dynamic activities rather than $[\text{H}^+]$, i.e., on $a_{\text{H}^+} = [\text{H}^+]f_{\text{H}^+}$. In dilute solution activity coefficient, f_{H^+} is near enough to unity and thus, $a_{\text{H}^+} = [\text{H}^+]$. At high concentrations, the activity coefficient is less than unity. Thus, pH defined by $-\log[\text{H}^+]$, which is not only of little theoretical significance, but it in fact cannot be measured directly. Therefore, pH is redefined as:

$$\text{pH} = -\log_{10} a_{\text{H}^+}$$

(This is what a pH meter reading is a measure of) i.e., pH of 10^2 M HCl cannot be calculated until f_{H^+} is known. Nevertheless, there is mathematically no basis for not having a negative pH.

ILLUSTRATION 8.19

What is the pH of the following solutions?

- 10^{-7} M NaOH
- 10^{-8} M NaOH
- 10^2 M NaOH

a. pH of 10^{-7} M NaOH

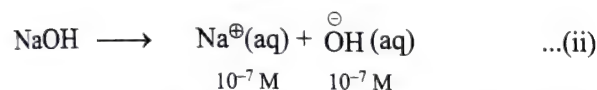
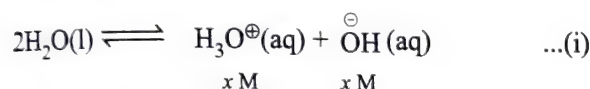
First method: The concentration of OH^- ions from pure water is 10^{-7} M. So add $[\text{OH}^-]$ from water and $[\text{OH}^-]$ from NaOH to get $[\text{OH}^-]_{\text{Total}}$.

$$\therefore [\text{OH}^-]_{\text{Total}} = 10^{-7} \text{ M} + 10^{-7} \text{ M} = 2 \times 10^{-7} \text{ M}$$

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-]_{\text{Total}} \\ &= -\log (2 \times 10^{-7}) \\ &= -\log 2 - \log 10^{-7} \\ &= -0.3011 + 7 = 6.6989 \\ \therefore \text{pH} &= 14 - 6.6989 = 7.3011 \end{aligned}$$

Second method: Due to common ion (OH^-), the suppression of ionisation of H_2O takes place in the presence of NaOH.

$$\text{Let } [\text{H}_3\text{O}^+] = [\text{OH}^-] = x \text{ M}$$



$[\text{H}_3\text{O}^+]_{\text{Total}}$ from equations (i) and (ii) = $(x + 10^{-7}) \text{ M}$.
At equilibrium

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14} = K_w$$

$$(x)(x + 10^{-7}) = 10^{-14}$$

$$\text{or } x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\therefore x = \frac{-10^{-7} + \sqrt{(10^{-7})^2 + (4 \times 10^{-14})}}{2}$$

$$\therefore [\text{H}_3\text{O}^+] = x = 0.616 \times 10^{-7} \text{ M}$$

Therefore, $[\text{OH}^-]_{\text{total}} = (10^{-7} + 0.616 \times 10^{-7}) \text{ M}$

$$\therefore \text{pOH} = -\log(1.616 \times 10^{-7}) = 6.7910$$

$$\text{pH} = 14 - 6.7910 = 7.209$$

b. pH of 10^{-8} M NaOH

First method:

$$\begin{aligned} [\text{OH}^-]_{\text{total}} &= 10^{-8} \text{ (from NaOH)} + 10^{-7} \text{ (from H}_2\text{O)} \\ &= 10^{-7} (10^{-1} + 1) = 1.1 \times 10^{-7} \end{aligned}$$

$$\text{pOH} = -\log (1.1 \times 10^{-7}) = -\log 1.1 - \log 10^{-7}$$

$$= -0.0414 + 7 = 6.9586$$

$$\text{pH} = 14 - 6.9586 = 7.0414.$$

Second method: Let $x = [\text{OH}^-] = [\text{H}_3\text{O}^+]$ from H_2O

The $[\text{OH}^-]_{\text{Total}}$ is generated from the ionisation of NaOH dissociated and from ionisation of H_2O .

$$\therefore K_w = (10^{-8} + x)(x) = 10^{-14}$$

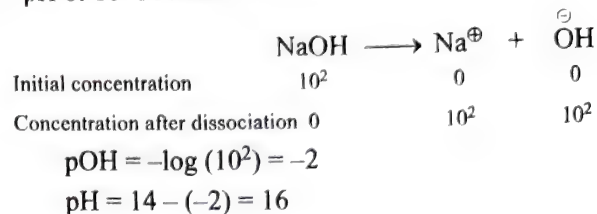
$$\text{or } x^2 + 10^{-8}x - 10^{-14} = 0$$

$$\therefore x = \frac{-10^{-8} + \sqrt{(10^{-8})^2 + (4 \times 10^{-14})}}{2}$$

$$[\text{H}_3\text{O}^+] = x = 9.5 \times 10^{-8}$$

$$\text{So, pH} = 7.02$$

c. pH of 10^2 M NaOH



$\text{pH} > 12$, only means that the $[\text{OH}^-] > 1 \text{ M}$. So pH scale becomes in between 2 and 16.

ILLUSTRATION 8.20

Calculate the percent error in the $[\text{H}_3\text{O}^+]$ made by neglecting the ionisation of water in 10^{-6} M NaOH solution.

Sol.

a. Neglecting the ionisation of H_2O , $[\text{OH}^-]$ from 10^{-6} M NaOH, and $[\text{H}_3\text{O}^+] = 10^{-8}$ M.

b. Including the ionisation of water

$$x = [\text{H}_3\text{O}^+] \text{ and } (x + 10^{-6}) = [\text{OH}^-]$$

$$\therefore (x + 10^{-6})(x) = 10^{-14} \text{ or } x^2 + 10^{-6}x - 10^{-14} = 0$$

$$\therefore x = \frac{-10^{-6} + \sqrt{10^{-12} + 4 \times 10^{-14}}}{2} = 9.9 \times 10^{-9}$$

$$\begin{aligned} \% \text{ error} &= \frac{(10^{-8}) - (9.9 \times 10^{-9})}{9.9 \times 10^{-9}} \times 100 \\ &= \frac{(10 \times 10^{-9}) - (9.9 \times 10^{-9})}{9.9 \times 10^{-9}} \times 100\% = 1\% \end{aligned}$$

ILLUSTRATION 8.21

The value of K_w at the physiological temperature 37°C is 2.4×10^{-14} . What is the pH at the neutral point of water at this temperature where there are equal numbers of H^+ and OH^- ions?

Sol. $[\text{H}^+] = \sqrt{2.4 \times 10^{-14}} = 1.55 \times 10^{-7}$

$$\text{pH} = -\log (1.55 \times 10^{-7}) = 6.81.$$

Thus, pH scale becomes in between 0 and 13.62.

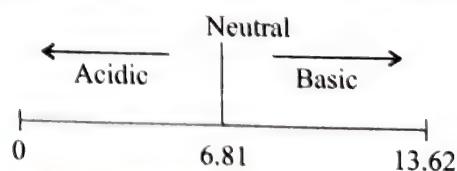


ILLUSTRATION 8.22

A solution of HCl has $\text{pH} = 5$. If 1 mL of it is diluted to 1 L. What will be the pH of resulting solution?

Sol. [Refer illustration 8.18(a)]

$$[\text{HCl}] = 10^{-5} \text{ M}$$

$$N_1 V_1 = N_2 V_2$$

$$10^{-5} \times 1 \text{ mL} = N_2 \times 1000 \text{ mL}$$

$$N_2 = \frac{10^{-5}}{1000 \text{ mL}} \approx 10^{-8} \text{ M}$$

$$\text{pH} = 6.98$$

CONCEPT APPLICATION EXERCISE 8.1**Objective Type**

1. 25.0 mL of 0.1 M NaOH is titrated with 0.1 M HCl. Calculate pH when:

i. 20 mL ii. 24 mL of acid is added.

- (1) 12.0, 11.30 (2) 11.30, 12
(3) 2.0, 2.70 (4) 2.70, 2.0

2. The conjugate acid of NH_2^- is

- (1) N_2H_4 (2) NH_3 (3) NH_2OH (4) NH_4^+

3. Which of the following will have pH close to 1.

- (1) 75 mL of M/5 HCl + 25 mL of M/5 NaOH
(2) 10 mL of M/10 HCl + 90 mL of M/10 NaOH
(3) 55 mL of M/10 HCl + 45 mL of M/10 NaOH
(4) 100 mL of M/10 HCl + 100 mL of M/10 NaOH

4. An acid solution of pH = 6 is diluted 100 times. The pH of solution becomes

- (1) 6.95 (2) 6 (3) 4 (4) 8

5. The number of H^+ ions present in 1 mL of solution having pH = 13 is

- (1) 6.023×10^{10} (2) 6.023×10^7
(3) 6.023×10^{13} (4) 10^{13}

6. Equal volumes of two solutions of HCl are mixed. One solution has a pH = 1, while the other has a pH = 5. The pH of the resulting solution is

- (1) <1 (2) Between 1 and 2
(3) 3 (4) Between 4 and 5

7. For pure water,

- (1) Both pH and pOH decrease with increase in temperature.
(2) Both pH and pOH increase with increase in temperature.
(3) pH decreases and pOH increases with increase in temperature.
(4) pH increases and pOH decreases with increase in temperature.

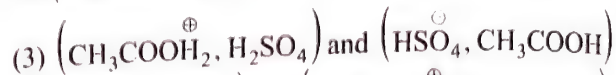
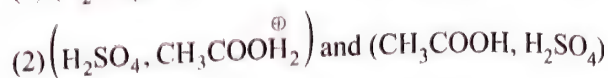
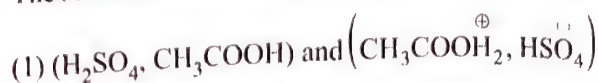
8. The pH of a solution increased from 3 to 6. Its $[\text{H}^+]$ will be

- (1) Reduced by 1000 times
(2) Increased to 1000 times
(3) Doubled
(4) Reduced to half

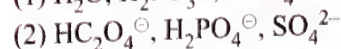
9. The following equilibria is established when H_2SO_4 is dissolved in acetic acid:



The set that characterised the conjugate acid-base pairs is:



10. Which of the following constitute a set of atmospheric species?



11. One litre of 0.5 M KCl is electrolysed by passing 9650 coulombs of electricity. The pH of resulting solution is

- (1) 1.0 (2) 2.0 (3) 7.0 (4) 13.0

12. pH of a solution made by mixing 200 mL of 0.0657 M NaOH, 140 mL of 0.107 M HCl and 160 mL of H_2O is

- (1) 3.04 (2) 2.43 (3) 2.74 (4) 2.27

13. When one drop of a concentrated HCl is added to 1 L of pure water at 25°C , the pH drops suddenly from 7 to 4. When the second drop of the same acid is added, the pH of the solution further drops to about

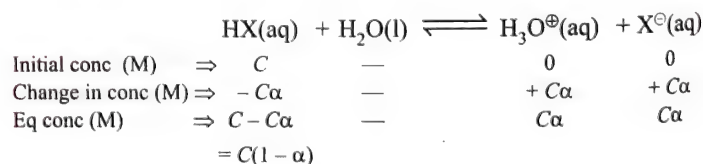
- (1) 0 (2) 1.0 (3) 2.0 (4) 3.7

ANSWERS

1. (1) 2. (2) 3. (1) 4. (1) 5. (2) 6. (2)
7. (1) 8. (1) 9. (3) 10. (1) 11. (4) 12. (2)
13. (4)

8.8 IONISATION CONSTANTS OF WEAK ACIDS

Consider a weak acid HX that is partially ionised in the aqueous solution. The equilibrium can be expressed by (if α is the extent of ionisation)



Here C = initial concentration of the undissociated acid, HX at time = 0,

α = extent upto which HX is ionised into ions.

Equilibrium constant (K_a) of weak acid is

$$K_a = \frac{C\alpha \times C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)^2} = C\alpha^2 \quad (1 - \alpha \approx 1) \quad \dots(i)$$

Note:

- a. The approximation $(1 - \alpha) \approx 1$ can be applied only if $\alpha < 0.05$ or $\alpha < 5\%$. If on solving problems by applying the

approximate formula α comes out to be $> 5\%$, the problems may be solved by applying exact formula and α may be calculated applying solution of quadratic equation:

$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

b. In general, if $K_a < 10^{-5}$ or $pK_a > 5$ and C is fairly high (generally 0.1 M or 0.01 M), then $(1 - \alpha)$ can be taken as unity.

c. If C is very low (i.e. for very dilute solutions), α is higher. In that case, $(1 - \alpha) \neq 1$. In such a case, quadratic equation is applied to solve α , i.e., $(1 - \alpha) K_a = C\alpha^2$

d. Basically, if decision on whether to go for approximation or not, is not easy, then just use approximation and solve but always remember to validate the approximation before reaching to a final answer.

Thus $pK_a = -\log [K_a]$,

$$\text{From equation (i), } K_a = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$$

$$\therefore [H_3O^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{\frac{C^2 K_a}{C}} = \sqrt{C \cdot K_a}$$

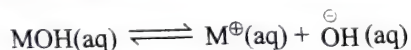
$$-\log [H_3O^+] = -\log (C\alpha) = -\log (C \cdot K_a)^{\frac{1}{2}}$$

$$pH = -\log (C\alpha) = \frac{1}{2} (pK_a - \log C)$$

$$\therefore pH_{\text{weak acid}} = \frac{1}{2} (pK_a - \log C)$$

8.8.1 IONISATION CONSTANTS OF WEAK BASES

The ionisation of weak base MOH can be represented by equation:



In a weak base there is a partial ionisation of MOH into M^+ and OH^- . The equilibrium constant for base ionization is called base ionization constant and is represented by K_b .

The equilibrium constant for weak base can be written similar to equilibrium constant of weak base,

$$K_b = \frac{C\alpha^2}{1 - \alpha} = C\alpha^2 (1 - \alpha \approx 1) \quad (\text{when } \alpha \text{ is very small}) \quad \dots(i)$$

Note: When $\alpha \geq 0.05$ or $\alpha \geq 5\%$ then the term $(1 - \alpha)$ is not taken as unity in equation (i)

Thus, $pK_b = -\log [K_b]$

From eq (i)

$$K_b = C\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_b}{C}}$$

$$[OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}} = \sqrt{\frac{C^2 K_b}{C}} = \sqrt{C \cdot K_b}$$

$$-\log [OH^-] = -\log (C\alpha) = -\log (C \cdot K_b)^{\frac{1}{2}}$$

$$pOH = -\log (C\alpha) = -\frac{1}{2} \log C - \frac{1}{2} \log K_b$$

$$= \frac{1}{2} (pK_b - \log C)$$

$$\therefore pOH_{\text{weak base}} = \frac{1}{2} (pK_b - \log C)$$

$$pH_{W.B.} = 14 - \left[\frac{1}{2} (pK_b - \log C) \right]$$

Many organic compounds like amines are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine (CH_3NH_2). Coedine, quinine and nicotine all behave as very weak bases due to their very small K_b . Ammonia produces OH^- ions in aqueous solution.



Table 8.4 The Ionisation Constants of some weak acids and weak bases (at 298 K)

Acid	Ionisation constants K_a	pK_a	Base	Ionisation constants K_b	pK_b
Hydrofluoric acid (HF)	3.5×10^{-4}	3.4559	Dimethylamine $[(CH_3)_2NH]$	5.4×10^{-4}	3.2676
Nitrous acid (HNO_2)	4.5×10^{-4}	3.3468	Triethyl amine $[(C_2H_5)_3N]$	6.45×10^{-5}	4.1904
Formic acid ($HCOOH$)	1.8×10^{-4}	3.7447	Ammonia (NH_3 or NH_4OH)	1.77×10^{-5}	4.752
Niacin (C_5H_4NCOOH)	1.5×10^{-5}	4.8239	Quinine (a plant product)	1.10×10^{-6}	5.9586
Acetic acid (CH_3COOH)	1.74×10^{-5}	4.7595	Pyridine (C_5H_5N)	1.77×10^{-9}	8.752
Benzoic acid ($PhCOOH$)	6.5×10^{-5}	4.1871	Urea $CO(NH_2)_2$	1.3×10^{-14}	13.8861
Hypochlorous acid ($HClO$)	3.0×10^{-8}	7.5229	Aniline ($PhNH_2$)	4.27×10^{-10}	9.3696
Hydrocyanic acid (HCN)	4.9×10^{-10}	9.3038			
Phenol ($PhOH$)	1.3×10^{-10}	9.8861			

Total $[H_3O^+]$ in mixture of two weak acids can be given as

$$[H_3O^+] = \sqrt{K_{a1} C_1 + K_{a2} C_2}$$

Total $[OH^-]$ in mixture of two weak bases

$$[OH^-] = \sqrt{K_{b1} C_1 + K_{b2} C_2}$$

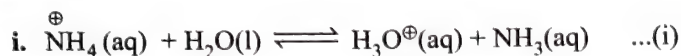
Total $[H_3O^+]$ in a mixture of weak acid and strong acid can be given as

$$[H_3O^+] = \frac{C_2 + \sqrt{C_2^2 + 4K_a C_1}}{2}$$

Where C_1 is the concentration (in mol/L) of the weak acid (ionization constant, K_a) and C_2 is that of strong acid. Accordingly pH can be calculated.

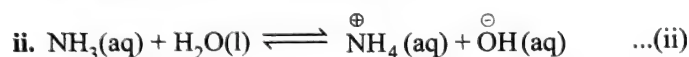
8.8.2 RELATION BETWEEN K_a AND K_b

K_a and K_b represent the strength of an acid and a base, respectively. The conjugate acid-base pair are related in a manner so that if one is known, the other can be deduced. For example in case of NH_4^+ and NH_3 ,



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

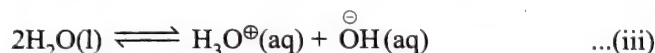
(K_a represents the strength of NH_4^+ as an acid)



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

(K_b represents the strength of NH_3 as a base)

iii. Adding equations (i) and (ii), the net equation is:



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \text{ M}$$

iv. Multiplying K_a and K_b , we get

$$\begin{aligned} K_a \times K_b &= \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= K_w = 10^{-14} \end{aligned}$$

Thus, $K_a \times K_b = K_w$

$$(5.6 \times 10^{-10})(1.8 \times 10^{-5}) = 10^{-14} \text{ M}$$

Therefore it can be generalised that "The equilibrium constant for a net reaction obtained after adding two or more reactions equals to the product of the equilibrium constants for individual reactions"

$$\therefore K_{\text{Net}} = K_1 \times K_2 \times \dots \quad \dots(\text{iv})$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \quad \dots(\text{v})$$

Taking negative logarithm both side of Eq. (v)

$$-\log(K_a) - \log(K_b) = -\log(K_w)$$

$$\therefore \text{p}K_a + \text{p}K_b = \text{p}K_w \text{ (at 298 K)} \quad \dots(\text{vi})$$

Therefore from Eqs. (v) and (vi), in case of a conjugate acid-base pair, knowing one, the other can be obtained.

$$\therefore K_b = \frac{K_w}{K_a} \quad \dots(\text{vii})$$

$$\text{and } K_a = \frac{K_w}{K_b} \quad \dots(\text{viii})$$

ILLUSTRATION 8.23

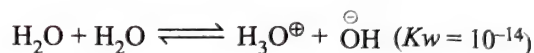
The ionisation constant of HF is 3.2×10^{-4} .

- Calculate the degree of dissociation of HF in its 0.02 M solution.
- Calculate the concentration of all species present (H_3O^+ , F^- and HF) in the solution.
- Calculate its pH.

Sol. First method:

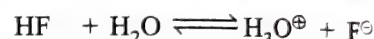
- The following proton transfer reactions are possible,
 $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- \quad (K_a = 3.2 \times 10^{-4})$

... (i)



... (ii)

Since $K_a \gg K_w$, reaction (i) is the main reaction.



Initial conc	\Rightarrow	0.02	—	0	0
Change in conc	\Rightarrow	-0.02α	—	$+0.02\alpha$	$+0.02\alpha$
Eq conc	\Rightarrow	$0.02 - 0.02\alpha$	—		
		$= 0.02(1 - \alpha)$		0.02α	0.02α

$$\therefore K_a = \frac{(0.02\alpha)^2}{0.02(1 - \alpha)} = \frac{0.02\alpha^2}{1 - \alpha} = 3.2 \times 10^{-4} \quad \dots(\text{i})$$

Solving the Eq. (i), the following quadratic equation is obtained,

$$\alpha^2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0.$$

$$\therefore \alpha = +0.12 \text{ and } -0.12. \quad (-\text{ve value is not taken})$$

Thus, $\alpha = 0.12$

$$\text{b. } [\text{H}_3\text{O}^+] = [\text{F}^-] = C\alpha = 0.02 \times 0.12 = 2.4 \times 10^{-3} \text{ M}$$

$$[\text{HF}] = C(1 - \alpha) = 0.02(1 - 0.12) = 1.76 \times 10^{-3} \text{ M}$$

$$\text{c. } \text{pH} = -\log[\text{H}^+] = -\log(2.4 \times 10^{-3}) = 2.62$$

Note: $\alpha = 0.12$ which is greater than 0.05, ($\alpha \geq 0.05$ or $\alpha \geq 5\%$). So the term $(1 - \alpha) \neq 1$, is taken.

Second method: By using formula of α , and pH.

$$\begin{aligned} \text{a. } \alpha &= \sqrt{\frac{K_a}{C}} = \sqrt{\frac{3.2 \times 10^{-4}}{0.02}} = \sqrt{16 \times 10^{-4} \times 10} \\ &= 4 \times 10^{-2} \times \sqrt{10} \\ &= 4 \times 3.162 \times 10^{-2} \\ &= 0.126 \end{aligned}$$

$$\therefore \alpha = 0.12$$

$$\text{b. } [\text{H}_3\text{O}^+] = [\text{F}^-] = C\alpha = 0.02 \times 0.12 = 2.4 \times 10^{-3} \text{ M}$$

$$[\text{HF}] = C(1 - \alpha) = 0.02(1 - 0.12) = 1.76 \times 10^{-3} \text{ M}$$

$$\begin{aligned} \text{c. } \text{p}K_a &= -\log(3.2 \times 10^{-4}) = -\log(32 \times 10^{-5}) \\ &= -\log(2^5 \times 10^{-5}) \\ &= -5 \log 2 + 5 \\ &= -5 \times 0.3 + 5 = 3.5 \end{aligned}$$

$$\text{p}K_a \approx 3.5$$

$$\begin{aligned}
 \text{pH} &= \frac{1}{2}(\text{p}K_a - \log C) = \frac{1}{2}(3.5 - \log 0.02) \\
 &= \frac{1}{2}(3.5 - \log 2 \times 10^{-2}) \\
 &= \frac{1}{2}(3.5 - 0.3 + 2) \\
 &= \frac{1}{2}(5.2) = 2.6
 \end{aligned}$$

$$\therefore \text{pH} \approx 2.6.$$

ILLUSTRATION 8.24

The pH of 0.1 M monobasic acid is 4.50. Calculate the concentration of species, H^+ , A^- , and HA at equilibrium. Also determine the value of K_a and $\text{p}K_a$ of the monobasic acid.

Use direct formula

$$\begin{aligned}
 \text{i. } \text{pH} &= \frac{1}{2}(\text{p}K_a - \log C) \\
 2 \text{pH} &= \text{p}K_a - \log C \\
 \therefore \text{p}K_a &= 2\text{pH} + \log C \\
 &= 2 \times 4.50 + \log 0.1 \\
 &= 9 - 1 = 8
 \end{aligned}$$

$$\therefore \text{p}K_a = 8.$$

$$\text{Hence, } K_a = 10^{-8}.$$

$$\begin{aligned}
 \text{ii. } \alpha &= \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-8}}{0.1}} = 10^{-4} \times \sqrt{10} = 3.162 \times 10^{-4} \\
 \therefore [\text{H}^+] &= [\text{A}^-] = C\alpha = 0.1 \times 3.16 \times 10^{-4} \\
 &= 3.16 \times 10^{-5} \text{ M} \\
 [\text{HA}]_{\text{eq}} &= C(1 - \alpha) \approx C = 0.1 \text{ M}
 \end{aligned}$$

ILLUSTRATION 8.25

Calculate the pH of 0.08 M solution of HOCl (hydrochlorous acid). The ionisation constant of the acid is 2.5×10^{-5} . Determine the percent dissociation of HOCl.

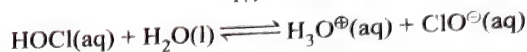
Using direct formula,

$$\begin{aligned}
 K_a &= 2.5 \times 10^{-5} = 25 \times 10^{-6} = (5)^2 \times 10^{-6} \\
 \text{p}K_a &= -\log[(5)^2 \times 10^{-6}] = -2 \log 5 + 6 \\
 &= -2 \times 0.7 + 6 = 4.6 \\
 \text{a. } \text{pH} &= \frac{1}{2}(\text{p}K_a - \log C) = \frac{1}{2}(4.6 - \log 0.08) \\
 &= \frac{1}{2}(4.6 - \log (2)^3 \times 10^{-2}) \\
 &= \frac{1}{2}[4.6 - 3 \times 0.3 + 2] \\
 &= 2.85
 \end{aligned}$$

$$\therefore \text{pH} = 2.85$$

$$\text{b. } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{25 \times 10^{-6}}{0.08}} = \sqrt{\frac{25 \times 10^{-6} \times 100}{8}}$$

$$\begin{aligned}
 &= \frac{\sqrt{25 \times 10^{-4}}}{2\sqrt{2}} \\
 &= \frac{5 \times 10^{-2}}{2 \times 1.414} = 0.017 \\
 &= 1.7 \times 10^{-3} \text{ M}
 \end{aligned}$$



Initial conc \Rightarrow	0.08	—	0	0
Conc at Eq \Rightarrow	$0.08(1-\alpha)$	—	$C\alpha$	$C\alpha$

$$\approx 0.08(1 - \alpha \approx 1)$$

$$\therefore [\text{HOCl}] = 0.08 \text{ M}$$

$$\begin{aligned}
 [\text{H}_3\text{O}^+] &= [\text{Cl}^-] = C\alpha = 0.08 \times 1.7 \times 10^{-3} \\
 &= 1.41 \times 10^{-3} \text{ M}
 \end{aligned}$$

$$\begin{aligned}
 \text{c. } \% \text{ dissociation} &= \frac{[\text{HOCl}]_{\text{dissociated}}}{[\text{HOCl}]_{\text{undissociated}}} \times 100 \\
 &= \frac{1.41 \times 10^{-3}}{0.08} \times 100 = 1.76\%
 \end{aligned}$$

ILLUSTRATION 8.26

The pH of 0.004 M hydrazine ($\text{NH}_2\cdot\text{NH}_2$) solution is 9.7. Calculate its ionisation constant K_b and $\text{p}K_b$.

Sol. Hydrazine is a weak base $\text{pH} = 9.7$

$$\therefore \text{pOH} = 14 - 9.7 = 4.3$$

$$2 \text{pOH} = 8.6$$

$$\text{a. } \text{pH}(\text{weak base}) = 14 - \left[\frac{1}{2}(\text{p}K_b - \log C) \right]$$

or

$$2\text{pOH}(\text{weak base}) = (\text{p}K_b - \log 0.004)$$

$$\text{p}K_b = 8.6 + \log 4 \times 10^{-3}$$

$$= 8.6 + 2 \log 2 - 3$$

$$= 8.6 + 2 \times 0.3 - 3$$

$$= 6.2$$

$$\therefore \text{p}K_b = 6.2$$

$$\text{b. } \text{p}K_b = -\log K_b = 6.2$$

$$\log K_b = -6.2 = -6 - 0.2 + 1 - 1 = \bar{7}.8$$

$$K_b = \text{Antilog}(\bar{7}.8) = 6.31 \times 10^{-7}.$$

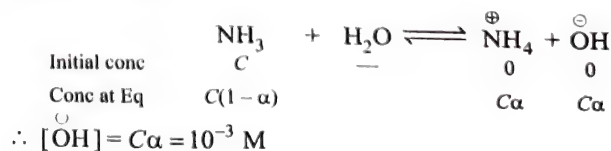
ILLUSTRATION 8.27

Determine the degree of dissociation of 0.05 M NH_3 at 25°C in a solution of $\text{pH} = 11$.

$$K_b = 1.77 \times 10^{-5} \quad (\text{p}K_b = 4.75)$$

Sol. NH_3 is a weak base, $\text{pH} = 11$, $\therefore \text{pOH} = 14 - 11 = 3$.

$$[\text{OH}^-] = 10^{-3} \text{ M}$$



$$\alpha = \frac{10^{-3}}{0.05} = 2 \times 10^{-2} \text{ or } 0.2\%$$

ILLUSTRATION 8.28

Calculate the ionic constant of the conjugate acid of NH_3 .

Given: $K_b = 1.77 \times 10^{-5}$

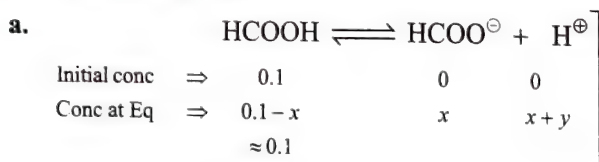
Sol. Ionic constant of conjugate acid (NH_4^+).

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.77 \times 10^{-5}} = 5.64 \times 10^{-10}$$

ILLUSTRATION 8.29

Calculate $[\text{H}^+]$ in a solution that is 0.1 M HCOOH and 0.1 M HOCN . $K_a(\text{HCOOH}) = 1.8 \times 10^{-4}$, $K_a(\text{HOCN}) = 3.3 \times 10^{-4}$.

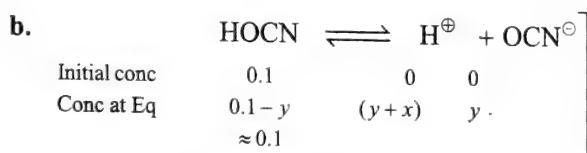
Sol. In the given problem, two weak acids both contribute to $[\text{H}^+]$, neither contributing such a big amount that the other share can be neglected.



$$K_{a1} = \frac{(x+y)(x)}{(0.1-x)} = 1.8 \times 10^{-4}$$

$$= \frac{(x+y)(x)}{0.1} = 1.8 \times 10^{-4} \quad \dots(i)$$

(y M of H^+ are contributed from HOCN).



(x M of H^+ are contributed from HCOOH)

$$K_{a2} = \frac{(y+x)(y)}{0.1} = 3.3 \times 10^{-4} \quad \dots(ii)$$

Divide equation (ii) by equation (i),

$$\frac{y}{x} = \frac{3.3}{1.8} = 1.83 \text{ or } y = 1.83x$$

Subtract equation (i) from equation (ii)

$$\frac{(x+y)y - x(x+y)}{0.1} = 1.5 \times 10^{-4}$$

$$\text{or } y^2 - x^2 = 1.5 \times 10^{-5} \quad \dots(iii)$$

Substitute $y = 1.83x$ in equation (iii) and solve to obtain,

$$x = 2.5 \times 10^{-3}, y = 1.83 \times x = 4.6 \times 10^{-3}$$

$$[\text{H}^+]_{\text{total}} = x + y = 7.1 \times 10^{-3}$$

Check of assumption: The values of x and y are slightly less than 10% of 0.1 M.

ILLUSTRATION 8.30

Determine the degree of ionisation and pH of 0.05M NH_3 solution k_b of $\text{NH}_3 = 1.77 \times 10^{-5}$. Calculate the ionisation constant of the conjugate acid (C_A) of NH_3 .

Sol. First method:

$$pk_b = 4.75$$

Since NH_3 is weak base, its pOH is given by the relation,

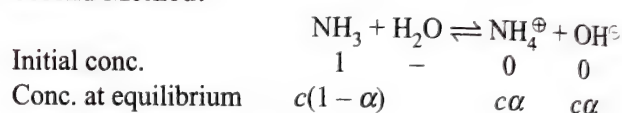
$$\begin{aligned} \text{pOH} &= \frac{1}{2} (pk_b - \log c) \\ &= \frac{1}{2} (4.75 - \log 0.05) \\ &= \frac{1}{2} (4.75 - \log 5 + \log 100) \\ &= \frac{1}{2} (4.75 - 0.7 + 2) [\log 5 \approx 0.7] \\ &= 3.025 \approx 3.03 \end{aligned}$$

$$\text{pH} = 14 - 13.03 = 10.97$$

Now, using the relation for conjugate acid-base pair, conjugate acid of NH_3 is NH_4^+ ion

$$\therefore k_a = k_w/k_b = 10^{-14}/1.77 \times 10^{-5} = 5.64 \times 10^{-10}$$

Second Method:



$$[\text{OH}^-] = c\alpha = 0.05\alpha$$

$$k_b = \frac{c\alpha^2}{[1-\alpha]} = \frac{0.05\alpha^2}{(1-\alpha)}$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation.

Thus,

$$k_b = c\alpha^2 \text{ or } \alpha = (1.77 \times 10^{-5}/0.05)^{1/2} = 0.018$$

$$[\text{OH}^-] = c\alpha = 0.005 \times 0.018 = 9.4 \times 10^{-4} \text{ M}$$

$$[\text{H}^+] = [\text{OH}^-] = 10^{-14}/(9.4 \times 10^{-4}) = 1.06 \times 10^{-11}$$

$$\text{pH} = -\log(1.06 \times 10^{-11}) = 10.97$$

The concentration of conjugate acid

NH_4^+ ion is:

$$k_a = k_w/k_b = 10^{-14}/(1.77 \times 10^{-5}) = 5.64 \times 10^{-10}$$

ILLUSTRATION 8.31

The K_a for formic acid and acetic acid are 2.1×10^{-4} and 1.1×10^{-5} , respectively. Calculate relative strength of acids.

Sol. Relative strength of weak acids = $\sqrt{\frac{K_{a1}}{K_{a2}}} \times \frac{C_1}{C_2}$

Assume C_1 and C_2 are same (although not given).

$$\therefore \text{Relative strength} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \sqrt{\frac{2.1 \times 10^{-4}}{1.1 \times 10^{-5}}} = 4.36:1$$

Relative strength for HCOOH to $\text{CH}_3\text{COOH} = 4.36:1$

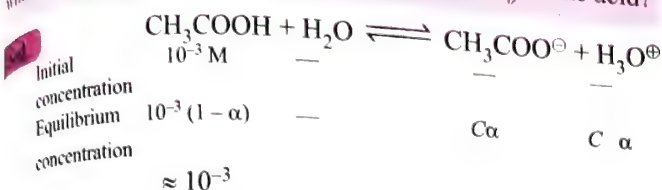
ILLUSTRATION 8.32

What is the pH of the solution when 100 mL of 0.1 M HCl is mixed with 100 mL of 0.1 M CH_3COOH ?

Sol. The diluted HCl is 0.1 M so that $\text{pH} = 1.00$.
With added strong acid present, the concentration of H^{\oplus} ions from ionisation of weak acid (CH_3COOH) is insignificant.

ILLUSTRATION 8.33

Calculate $[\text{H}^{\oplus}]$ and $[\text{OH}^-]$ in 10^{-3} M solution of monobasic acid which is 4.0% ionised. What is the pH , K_a and $\text{p}K_b$ of the acid?



Given $\alpha = \frac{4.0}{100} = 4 \times 10^{-2}$

a. $[\text{H}_3\text{O}^{\oplus}] = C\alpha = 10^{-3} \times 4 \times 10^{-2} = 4 \times 10^{-5}$

$\text{pH} = -\log(4 \times 10^{-5}) = -2 \log 2 + 5$
 $= -2 \times 0.3 + 5 = 4.4$

$\therefore \text{pH} = 4.4$

b. $\text{pOH} = 14 - 4.4 = 9.6$

$-\log [\text{OH}^-] = 9.6, \log [\text{OH}^-]$
 $= -9.6$

$= -9 - 0.6 + 1 - 1 = -10.4$

$\therefore [\text{OH}^-] = 2.5 \times 10^{-10}$ M

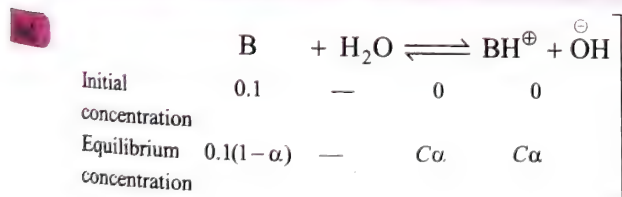
c. $K_a = C\alpha^2 = 10^{-3} \times (4 \times 10^{-2})^2 = 1.6 \times 10^{-6}$

$\text{p}K_a = -\log(1.6 \times 10^{-6}) = -\log(16 \times 10^{-7})$
 $= -4 \log 2 + 7$
 $= -1.2 + 7 = 5.8$

$\therefore \text{p}K_a = 5.8$

ILLUSTRATION 8.34

Calculate $[\text{H}^{\oplus}]$ and $[\text{OH}^-]$ in a 0.1 M solution of weak monoacidic base which is 2.0% ionised. What is the pH of solution?



Given $\alpha = \frac{2.0}{100} = 2 \times 10^{-2}$

$[\text{OH}^-] = C\alpha = 0.1 \times 2 \times 10^{-2} = 2 \times 10^{-3}$ M

$\text{pOH} = -\log(2 \times 10^{-3}) = -0.3 + 3 = 2.7$

$\text{pH} = 14 - 2.7 = 11.3$

ILLUSTRATION 8.35

The pH of pure water at 25°C and 35°C are 7 and 6, respectively. Calculate the heat of formation of water from H^{\oplus} and OH^- .

Sol. At 25°C : $[\text{H}^{\oplus}] = 10^{-7}$; $\therefore K_w = 10^{-14}$

At 35°C : $[\text{H}^{\oplus}] = 10^{-6}$; $\therefore K_w = 10^{-12}$

Now using

$$2.303 \log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$2.303 \log \frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2 \text{ cal}} \left[\frac{10}{298 \times 308} \right]$$

$$\Delta H = 84551.4 \text{ cal mol}^{-1} = 84.551 \text{ kcal mol}^{-1}$$

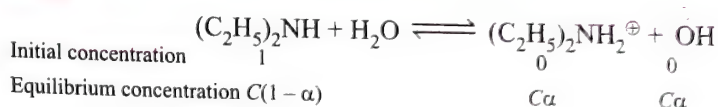
Thus, $\text{H}_2\text{O} \rightleftharpoons \text{H}^{\oplus} + \text{OH}^-$;
 $\Delta H = 84.551 \text{ kcal mol}^{-1}$

$\therefore \text{H}^{\oplus} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$;
 $\Delta H = -84.551 \text{ kcal mol}^{-1}$

ILLUSTRATION 8.36

The pH of 0.05 M aqueous solution of diethyl amine is 12.0. Calculate K_b .

Sol. Diethyl amine is base and gives OH^- as



$\therefore [\text{OH}^-] = C\alpha$ where C is concentration of base and $C = 0.05$ M

$\text{pH} = 12$

$\therefore \text{pOH} = 2$

or $[\text{OH}^-] = 10^{-12}$ M

$\therefore C\alpha = 10^{-2}$

or $0.05 \times \alpha = 10^{-2}$

($C = 0.05$)

$\therefore \alpha = 0.2$

Now for a base,

$$K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.05 \times (0.2)^2}{(1-0.2)} = \frac{0.05 \times 0.04}{0.8} = 2.5 \times 10^{-3}$$

Note: Do not use $K_b = C\alpha^2$ since $\alpha = 0.2$ and $1 - \alpha = 0.8$.

If α would have been very small, then the direct formula can be used to calculate K_b of weak base.

$$\text{pOH} = \frac{1}{2} (\text{p}K_b - \log C)$$

8.9 COMMON ION EFFECT IN THE IONISATION OF ACIDS AND BASES

Common ion effect is defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. This is based on Le Chatelier's principle. For example, consider the dissociation equilibrium of acetic acid (CH_3COOH), represented as HAc .



$$K_a = \frac{[\text{H}^{\oplus}][\text{Ac}^-]}{[\text{HAc}]}$$

On addition of acetate ions (Ac^-) to an acetic acid solution, $[\text{H}^{\oplus}]$ decreases. Also if H^{\oplus} ions are added from an external source, then the equilibrium moves in the direction of undissociated acetic

acid, i.e., in a direction of reducing the concentration of H^+ ions. This is called common ion effect.

For example, on addition of 0.05 M acetate ion to 0.05 M acetic acid solution, the pH of the solution will be: (K_a of HAc = 1.8×10^{-5})

		$HAc \rightleftharpoons H^+(aq) + Ac^-(aq)$		
Initial concentration	\Rightarrow	0.05	0	0.05
Change in concentration	\Rightarrow	-x	+x	+x
Equilibrium concentration	\Rightarrow	0.05-x	x	(0.05+x)

Therefore,

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = \frac{(x)(0.05+x)}{(0.05-x)} = 1.8 \times 10^{-5}$$

As K_a is small for a weak acid $x \ll 0.05$

Hence, $(0.05+x) \approx (0.05-x) \approx 0.05$.

$$\text{Thus, } \frac{(x)(0.05)}{(0.05)} = 1.8 \times 10^{-5}, \Rightarrow x = [H^+] = 1.8 \times 10^{-5} \text{ M}$$

$$\therefore \text{pH} = -\log(1.8 \times 10^{-5}) = 4.74.$$

Note: When same concentration of the common ion is added to the same concentration of weak acid or weak base, there is no change in pH of weak acid or weak base.

ILLUSTRATION 8.37

Calculate the pH of 0.1 M NH_3 solution.

Sol. NH_3 is a weak base,

$$\begin{aligned} \therefore \text{pOH}_{\text{weak base}} &= \frac{1}{2} (\text{p}K_b - \log C) \\ &= \frac{1}{2} (4.76 - \log 0.1) \\ &= \frac{1}{2} (4.76 + 1) = 2.88 \end{aligned}$$

$$\therefore \text{pH}_{\text{weak base}} = 14 - 2.88 = 11.12$$

ILLUSTRATION 8.38

Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.1 M HCl.

Given: K_b for $NH_3 = 1.77 \times 10^{-5}$ ($\text{p}K_b \approx 4.76$)

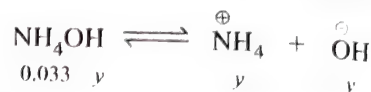
Sol. On addition of 25 mL of 0.1 M HCl (2.5 mmoles), to 50 mL of 0.1 M NH_3 (5.0 mmoles), 2.5 mmoles of NH_3 molecules are neutralised. The resulting 75 mL (25 mL + 50 mL) solution contains the remaining unneutralised 2.5 mmoles of NH_3 molecules and 2.5 mmoles of NH_4^+ ions.

	$NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$			
mmoles initially	5.0 mmol	2.5 mmol	0	0
mmoles at equilibrium	(5 - 2.5) = 2.5	2.5 - 2.5 = 0	2.5	2.5

$$[NH_4^+]_{eq} = \frac{2.5 \text{ mmoles}}{75 \text{ mL}} = 0.033 \text{ M}$$

$$[NH_3]_{eq}(\text{unreacted}) = \frac{2.5 \text{ mmol}}{75 \text{ mL}} = 0.033 \text{ M}$$

This NH_3 exists in the following equilibrium:



$$\therefore [NH_4^+]_{total} = 0.033 + y \approx 0.033 \text{ (as } y \text{ is small)}$$

$$[NH_3] = 0.033 - y \approx 0.033 \text{ (as } y \text{ is small)}$$

$$\therefore K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.033)[OH^-]}{(0.033)} = 1.77 \times 10^{-5}$$

$$\therefore [OH^-] = 1.77 \times 10^{-5}$$

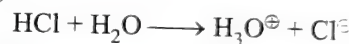
$$\text{pOH} = -\log(1.77 \times 10^{-5}) = 4.76$$

$$\therefore \text{pH} = 14 - 4.76 = 9.24$$

ILLUSTRATION 8.39

What is the pH of a solution containing 0.01 M?

Sol. HCl is strong acid and it is completely ionised (100% ionisation)



$$[H^+] = \frac{0.01}{1 \text{ L}} = 10^{-2} \text{ M} \therefore \text{pH} = 2.0$$

ILLUSTRATION 8.40

Calculate the change in pH if 0.02 mol CH_3COONa is added to 1.0 L of this solution.

(K_a of $CH_3COOH = 1.8 \times 10^{-5}$)

Sol. CH_3COONa contains CH_3COO^- ions which react with H_3O^+ ion from HCl. Assume complete reaction of H_3O^+ with CH_3COO^- ion.

	$CH_3COO^- + H_3O^+ \longrightarrow CH_3COOH + H_2O$			
Initial concentration	\Rightarrow 0.02 M	0.01 M	—	—
Concentration reacted	\Rightarrow 0.02 - 0.01	0.01	—	—
Final concentration	\Rightarrow 0.01(excess)	0	0.01	0.01



$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(0.01)[H_3O^+]}{(0.01)} = 1.8 \times 10^{-5}$$

$$\therefore [H_3O^+] = 1.8 \times 10^{-5}, \text{ so } \text{pH} = 4.74$$

$$\text{Change in pH } (\Delta \text{pH}) = 4.74 - 2.00 = 2.74$$

ILLUSTRATION 8.41

0.1 M NH_3 solution is found to have a $[OH^-]$ of $1.33 \times 10^{-3} \text{ M}$.

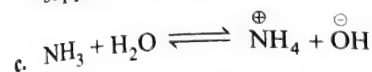
- What is the pH of the solution?
- What will be the pH of the solution after 0.1 M NaOH is added to it?
- Calculate K_b and $\text{p}K_b$ for NH_3 .
- How will NaOH added to the solution affect the extent of dissociation of NH_3 ?

a. $[\text{OH}^-] = 1.33 \times 10^{-3}$, $\text{pOH} = 2.88$

$\therefore \text{pH} = 14 - 2.88 = 11.12$

b. $[\text{OH}^-] = 0.1 \text{ M}$, $\text{pOH} = 1 \therefore \text{pH} = 14 - 1 = 13$.

The $[\text{OH}^-]$ from NH_3 is negligible, since NaOH suppresses the dissociation of the weak base.



$\therefore K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

$= \frac{(1.33 \times 10^{-3})(1.33 \times 10^{-3})}{0.1 - 0.00133} [0.1 - 0.00133 \approx 0.1]$

$= \frac{(1.33 \times 10^{-3})^2}{0.1}$

$= 1.79 \times 10^{-5} \approx 1.8 \times 10^{-5}$

$\therefore \text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.7447$

ILLUSTRATION 8.42

The self ionisation constant for pure HCOOH , $K = [\text{HCOOH}_2^+][\text{HCOO}^-]$ is 10^{-6} at room temperature. What percentage of HCOOH molecules are converted to HCOO^- ions. The density of HCOOH is 1.22 g cm^{-3} .



$K_a = [\text{HCOOH}_2^+][\text{HCOO}^-] = 10^{-6}$

$\therefore [\text{HCOOH}_2^+] = [\text{HCOO}^-] = 10^{-3} \text{ M}$

(Since each ion is produced in equal number of moles)

Initial moles of HCOOH

$= \left(\frac{1.22 \text{ g}}{\text{cm}^3} \right) \left(\frac{10^3 \text{ cm}^3}{\text{L}} \right) \left(\frac{1 \text{ mol HCOOH}}{46.0 \text{ g HCOOH}} \right)$

$= \frac{1.22 \times 10^3 \times 1}{46} = 26.5 \text{ mol L}^{-1} = 26.5 \text{ M}$

% dissociated to HCOO^- ion

$= \left(\frac{10^{-3}}{26.5} \right) \times 100\% = 0.004\%$

ILLUSTRATION 8.43

Liquid NH_3 ionises to a slight extent. At -50°C , its ionic product $K_{\text{NH}_3} = [\text{NH}_4^+][\text{NH}_2^-]$ is 10^{-30} . How many amide ions, NH_2^- are present per mm^3 of pure liquid NH_3 ?



$K_{\text{NH}_3} = [\text{NH}_4^+][\text{NH}_2^-] = 10^{-30}$

Since each ion is produced in equal number of moles

$\therefore [\text{NH}_2^-] = [\text{NH}_4^+] = 10^{-15} \text{ M}$

Number of ions/ mm^3

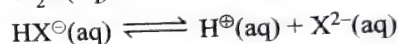
$= \left(\frac{10^{-15} \text{ mol}}{\text{L}} \right) \left(\frac{1 \text{ L}}{10^6 \text{ mm}^3} \right) \left(\frac{6 \times 10^{23} \text{ ions}}{\text{mol}} \right)$

$= \frac{10^{-15} \times 1 \times 6 \times 10^{23}}{10^6} = 600 \text{ ions mm}^{-3}$

8.10 DI- AND POLYBASIC ACIDS AND DI- AND POLYACIDIC BASES

Acids which have more than one ionisable proton per molecule of acids are known as polybasic or polyprotic acids, e.g., oxalic acid (HOOC-COOH), H_2SO_4 , and H_3PO_4 .

The ionisation reactions for a dibasic acid, H_2X are represented as:



The corresponding equilibrium constants are as:

$K_{a1} = \frac{[\text{H}^+][\text{HX}^-]}{[\text{H}_2\text{X}]}$ and $K_{a2} = \frac{[\text{H}^+][\text{X}^{2-}]}{[\text{HX}^-]}$

(K_{a1} and K_{a2} are called first and second ionisation constants, respectively, of the acid H_2X).

Similarly, for tribasic acids such as H_3PO_4 , there are three ionisation constants.

It is found that K_{a1} of polyprotic acid is greater than K_{a2} or K_{a3} (i.e., $K_{a1} > K_{a2} > K_{a3}$), because it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. Similarly, it is more difficult to remove a proton from a doubly charged anion as compared to single charged anion.

The primary reaction involves the dissociation of H_2X and H_3O^+ in the solution comes mainly from the first dissociation step.

Table 8.5 The ionisation constants of some polyprotic acids (298 K)

Acid	K_{a1}	K_{a2}	K_{a3}
Oxalic acid $[(\text{COOH})_2]$	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous acid (H_2SO_3)	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric acid (H_2SO_4)	Very large	1.2×10^{-2}	
Carbonic acid (H_2CO_3)	4.3×10^{-7}	5.6×10^{-11}	
Citric acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric acid (H_3PO_4)	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

ILLUSTRATION 8.44

Find the concentration of H^+ , HCO_3^- , and CO_3^{2-} in a 0.01 M solution of carbonic acid if the pH of solution is 4.18.

$K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$

Sol. Given, $\text{pH} = 4.18 = -\log [\text{H}^+]$

$$\therefore [\text{H}^+] = 6.61 \times 10^{-5} \text{ mol L}^{-1}$$

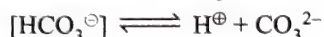


$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\text{or } 4.45 \times 10^{-7} = \frac{[6.61 \times 10^{-5}][\text{HCO}_3^-]}{[0.01]}$$

$$\text{or } [\text{HCO}_3^-] = 6.73 \times 10^{-5} \text{ mol L}^{-1}$$

Again for dissociation of HCO_3^- , we have



$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\text{or } 4.69 \times 10^{-11} = \frac{[6.61 \times 10^{-5}][\text{CO}_3^{2-}]}{[6.73 \times 10^{-5}]}$$

$$[\text{CO}_3^{2-}] = 4.78 \times 10^{-11} \text{ mol L}^{-1}$$

ILLUSTRATION 8.45

K_1 and K_2 for dissociation of H_2S are 4×10^{-3} and 1×10^{-5} . Calculate sulphide ion concentration in 0.1 M H_2S solution. Also report $[\text{H}^+]$ and pH .

Sol. $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$

$$K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 4 \times 10^{-3}$$

$$[\text{H}^+] = C\alpha, \quad [\text{HS}^-] = C\alpha, \quad [\text{H}_2\text{S}] = C(1 - \alpha)$$

$$\text{or } 4 \times 10^{-3} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

$$\text{or } 4 \times 10^{-3} = \frac{0.1 \times \alpha^2}{(1 - \alpha)} \quad (1 - \alpha \text{ should not be neglected})$$

$$\therefore \alpha = 0.18; \therefore [\text{H}^+] = C\alpha = 0.1 \times 0.18 = 0.018 \text{ M}$$

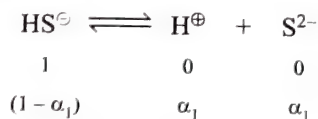
$$\therefore \text{pH} = 1.7447$$

$$[\text{HS}^-] = C\alpha = 0.1 \times 0.18 = 0.018 \text{ M}$$

$$[\text{H}_2\text{S}] = C(1 - \alpha) = 0.1(1 - 0.18) = 0.082 \text{ M}$$

Now, HS^- further dissociates to H^+ and S^{2-} ;

$$C_1 = [\text{HS}^-] = 0.018 \text{ M}$$



$$\therefore K_2 = 1 \times 10^{-5} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

Because $[\text{H}^+]$ already in solution = 0.018 and thus, dissociation of HS^- further suppresses due to common ion effect and $1 - \alpha \approx 1$.

$$\therefore 1 \times 10^{-5} = \frac{0.018 \times C_1 \alpha_1}{C_1 (1 - \alpha_1)} = 0.018 \times \alpha_1$$

$$\therefore \alpha_1 = \frac{1 \times 10^{-5}}{0.018} = 5.55 \times 10^{-4}$$

$$\therefore [\text{S}^{2-}] = C_1 \alpha_1 = 0.018 \times 5.55 \times 10^{-4} = 10^{-5}$$

$$\therefore [\text{HS}^-] = C_1 (1 - \alpha_1) = C_1 = 0.018 \text{ M}$$

ILLUSTRATION 8.46

Calculate the concentration of all species of significant concentrations present in 0.1 M H_3PO_4 solution.

$$(K_1 = 7.5 \times 10^{-3}, K_2 = 6.2 \times 10^{-8}, K_3 = 3.6 \times 10^{-13})$$

Sol. Step I $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$

$$K_1 = 7.5 \times 10^{-3}$$

Step II $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$

$$K_2 = 6.2 \times 10^{-4}$$

Step III $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$

$$K_3 = 3.6 \times 10^{-13}$$

For Step I: $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$

$$\begin{array}{ccc} 0.1 & 0 & 0 \\ 0.1 - C & C & C \end{array}$$

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{C \cdot C}{(0.1 - C)}$$

$$7.5 \times 10^{-3} = \frac{C^2}{(0.1 - C)}$$

$$\therefore C = 0.024 \text{ and } [\text{H}^+] = 0.024 \text{ M}, \quad [\text{H}_2\text{PO}_4^-] = 0.024 \text{ M}, \quad [\text{H}_3\text{PO}_4] = 0.1 - 0.024 = 0.076 \text{ M}$$

The value of K_1 is much larger than K_2 and K_3 .

Also dissociation of steps II and III occurs in presence of H^+ furnished in step I and thus, dissociation of steps II and III is further suppressed due to common effect.

For Step II: $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$

$$\begin{array}{ccc} 0.024 & 0.024 & 0 \\ (0.024 - y) & (0.024 + y) & y \end{array}$$

The dissociation of H_2PO_4^- occurs in presence of $[\text{H}^+]$ furnished in Step I.

$$\text{Thus, } K_2 = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\text{or } 6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)} \text{ because } y \text{ is small.}$$

Assuming $0.024 - y \approx 0.024$ and neglecting y^2

$$\therefore 6.2 \times 10^{-8} = \frac{0.024y}{0.024}$$

$$\therefore y = 6.2 \times 10^{-8}$$

$$\text{or } [\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ [Insignificant]}$$

For Step III: $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$

$$\begin{array}{ccc} (6.2 \times 10^{-8} - x) & (0.024 + x) & x \end{array}$$

$$\therefore K_3 = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = \frac{(0.024 + x)x}{[(6.2 \times 10^{-8}) - x]}$$

Again neglecting x^2 and assuming $(6.2 \times 10^{-8}) - x \approx 6.2 \times 10^{-8}$

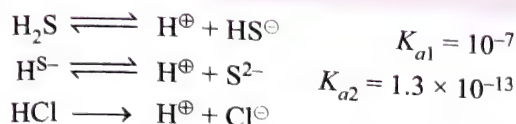
$$\therefore 3.6 \times 10^{-13} = \frac{0.024x}{6.2 \times 10^{-8}}$$

$$\therefore x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-18}}{0.024} = 9.3 \times 10^{-19}$$

[Insignificant]

ILLUSTRATION 8.47

A solution contains 0.1 M H_2S and 0.3 M HCl . Calculate the concentration of S^{2-} and HS^- ions in solution. Given K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13} , respectively.



Due to common ion effect, the dissociation of H_2S is suppressed and $[\text{H}^+]$ in solution is due to HCl .

$$\therefore K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$10^{-7} = \frac{(0.3)[\text{HS}^-]}{[0.1]} \quad ([\text{H}^+] \text{ from HCl} = 0.3)$$

$$\therefore [\text{HS}^-] = \frac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8} \text{ M}$$

$$\text{Further } K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \text{ and } K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$\therefore K_{a1} \times K_{a2} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[0.3]^2 [\text{S}^{2-}]}{[0.1]}$$

$$\therefore [\text{S}^{2-}] = \frac{1.3 \times 10^{-20} \times 0.1}{0.09} = 1.44 \times 10^{-20} \text{ M}$$

CONCEPT APPLICATION EXERCISE 8.2**Objective Type:**

1. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6} \text{ M}$. What is the value of K_w at 90°C .

- (1) 10^{-6} (2) 10^{-8} (3) 10^{-12} (4) 10^{-14}

2. HCOOH and CH_3COOH solutions have equal pH. If K_1/K_2 is 4, the ratio of their molar concentration will be

- (1) 0.25 (2) 0.5 (3) 2 (4) 4

3. $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$, $K_w = 10^{-14}$ at 25°C , hence K_a is

- (1) 10^{-7} (2) 5.55×10^{-13}

- (3) 10^{-14} (4) 18×10^{-17}

4. Which of the following expression is wrong?

- (1) $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ for a neutral solution at all temperatures.

- (2) $[\text{H}^+] < \sqrt{K_w}$ and $[\text{OH}^-] > \sqrt{K_w}$ for basic solution

(3) $[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w}$ for a neutral solution

(4) $[\text{H}^+] > \sqrt{K_w}$ and $[\text{OH}^-] < \sqrt{K_w}$ for an acidic solution

5. For a 'C' M concentrated solution of a weak electrolyte A_xB_y , α (degree of dissociation) is

- (1) $\sqrt{K_{eq}/xyC}$ (2) $[K_{eq} \cdot C/(xy)]^{1/2}$

- (3) $(K_{eq}/C^{x+y-1} \cdot x^x y^y)^{1/(x+y)}$ (4) $[K_{eq}/C(x+y)]^{1/2}$

6. K_b for NH_4OH is 1.8×10^{-5} . The $[\text{OH}^-]$ of 0.1 M NH_4OH is

- (1) 5.0×10^{-2} (2) 4.20×10^{-3}

- (3) 1.34×10^{-3} (4) 1.8×10^{-6}

7. The dissociation constant of monobasic acids A, B, C and D are 6×10^{-4} , 5×10^{-5} , 3.6×10^{-6} , and 7×10^{-10} , respectively. The pH values of their 0.1 M aqueous solution are in the order:

- (1) $D > C > B > A$ (2) $A > B > C > D$

- (3) $A = B = C = D$ (4) None

8. The molarity of NH_3 of pH = 12 at 25°C is

- (1) 1.8×10^{-5}

- (1) 11.7 M (2) 5.5 M

- (3) 0.55 M (4) 0.01 M

9. K_a of HA at 25° is 10^{-5} . If 0.1 mol of this acid is dissolved in 1 L of aqueous solution, the percent dissociation at equilibrium will be closer to

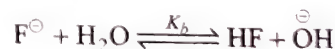
- (1) 0.1% (2) 1.0% (3) 99.0% (4) 99.9%

10. For a polyprotic acid, H_3PO_4 , its three dissociation constants K_1 , K_2 , and K_3 are in the order

- (1) $K_1 = K_2 > K_3$ (2) $K_1 = K_2 = K_3$

- (3) $K_1 > K_2 > K_3$ (4) $K_1 < K_2 < K_3$

11. Given $\text{HF} + \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{H}_3\text{O}^+ + \text{F}^-$



Which relation is correct?

- (1) $K_b = K_w$ (2) $K_a \times K_b = K_w$

- (3) $K_b = \frac{1}{K_w}$ (4) $\frac{K_a}{K_b} = K_w$

12. K_a of HA is 10^{-4} . The equilibrium constant for its reaction with a strong base is

- (1) 10^{-14} (2) 10^{-9} (3) 10^{-10} (4) 10^{10}

13. The percentage error in $[\text{H}^+]$ provided by 10^{-8} M HCl , if ionisation of water is not neglected, is

- (1) 2% (2) 3% (3) 4% (4) 5%

14. H_3BO_3 is:

- (1) Monobasic and weak Lewis acid
(2) Monobasic and weak Brønsted acid
(3) Tribasic and weak Brønsted acid
(4) Monobasic and strong Lewis acid

15. The enthalpy change for first proton neutralisation of H_2S is $-37.1 \text{ kJ mol}^{-1}$. What is the enthalpy change for first ionisation of H_2S .
 (1) 94.2 (2) -20.0 (3) 20.0 (4) -94.2
16. The factor by which the degree of ionisation of 200 mL of 0.1 M benzoic acid solution ($K_a = 4 \times 10^{-5}$) changes on addition of 100 mL of 0.2 M HCl is:
 (1) 0.02 (2) 0.03 (3) 33.33 (4) None
17. The concentration of CO_2 in atmosphere is 88 ppm. If all of the CO_2 present in 10^5 mL of air is dissolved in 1 dm^3 water, then approximate pOH of solution at 27°C will be ($K_{a1} = 10^{-7}$, $K_{a2} = 10^{-11}$ for H_2CO_3)
 (1) 3.2 (2) 3.85 (3) 10.15 (4) None
18. A solution of a weak monoprotic acid has dissociation constant K_a . The minimum initial concentration C such that the concentration of the undissociated acid can be equated to C within an error of 1% would be
 (1) $9900K_a$ (2) $10000K_a$ (3) $99K_a$ (4) K_a
19. Two weak acids HX and HY have K_a values 1.75×10^{-5} and 1.3×10^{-5} , respectively, at a certain temperature. An equimolar solution of mixture of two acids is partially neutralised by NaOH. How is the ratio of the contents of X^\ominus and Y^\ominus ions related to the K_a values and molarity?

$$(1) \left[\frac{\alpha}{1-\alpha} \right] = \frac{1.75}{1.3} \times \left[\frac{\alpha'}{1-\alpha'} \right], 0, \text{ where } \alpha \text{ and } \alpha' \text{ are}$$

ionised fractions of the acids HX and HY respectively.

- (2) The ratio is unrelated to the K_a values.
 (3) The ratio is unrelated to the molarity.
 (4) The ratio is unrelated to the pH of the solution.
20. H_2S behaves as a weak diprotic acid in aqueous solution. Which of the following is the correct explanation for pH of a solution of H_2S in terms of its pK_1 , pK_2 , $[\text{H}_2\text{S}]$ and $[\text{S}^{2-}]$

$$(1) \text{pH} = \frac{1}{2} (pK_1 + pK_2)$$

$$(2) \text{pH} = \frac{1}{2} \left(pK_1 + pK_2 - \log \frac{[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \right)$$

$$(3) \text{pH} = \frac{1}{2} \left(pK_1 + pK_2 + \log \frac{[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \right)$$

$$(4) \text{pH} = \frac{1}{2} \left(pK_1 - pK_2 + \log \frac{[\text{H}_2\text{S}]}{[\text{S}^{2-}]} \right)$$

ANSWERS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (3) | 2. (1) | 3. (4) | 4. (1) | 5. (3) |
| 6. (3) | 7. (1) | 8. (3) | 9. (2) | 10. (3) |
| 11. (2) | 12. (4) | 13. (4) | 14. (1) | 15. (3) |
| 16. (2) | 17. (3) | 18. (1) | 19. (1) | 20. (3) |

8.11 BUFFER SOLUTION

A buffer solution is defined as a solution which resists any change in its pH value on addition of small amount of strong acid or strong base to it.

The preservation of a solution of definite pH is difficult. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in glass apparatus, the alkaline impurities present in glass may dissolve into the solution and may alter its pH.

8.11.1 TYPES OF BUFFER SOLUTION

There are two types of buffer solution. These are:

a. Solutions of single substances: The solution of the salt of a weak acid (W_A) and weak base (W_B) e.g., ammonium acetate ($\text{CH}_3\text{COONH}_4$), ammonium benzoate (PhCOONH_4), acts as a buffer.

b. Solutions of Mixtures: These are further of two types:

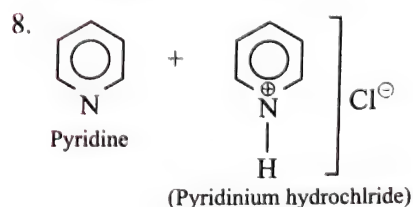
i. Acidic buffer: These are solutions of a mixture of weak acid (W_A) and a salt of weak acid with a strong base. (W_A/S_B)

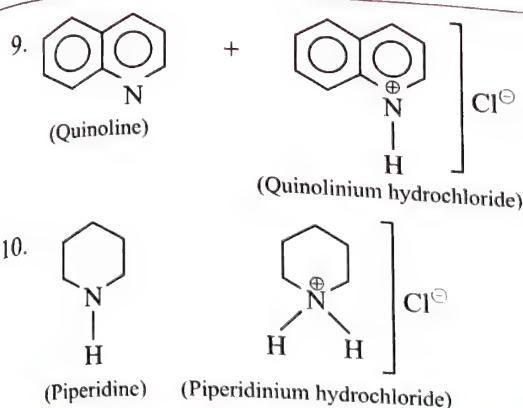
- $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- $\text{CH}_3\text{COOH} + \text{CH}_3\text{COOK}$
- $\text{HCN} + \text{NaCN}$
- $\text{HCN} + \text{Ca}(\text{CN})_2$
- $\text{PhCOOH} + \text{PhCOONa}$
- $\text{H}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$
- $\text{H}_3\text{PO}_4 + \text{Na}_2\text{HPO}_4$
- $\text{H}_3\text{PO}_4 + \text{Na}_3\text{PO}_4$
- $\text{H}_3\text{BO}_3 + \text{NaH}_2\text{BO}_3$
- $\text{H}_3\text{PO}_3 + \text{NaH}_2\text{PO}_3$
- $\text{H}_3\text{PO}_3 + \text{Na}_2\text{HPO}_3$
- $\text{H}_3\text{PO}_2 + \text{NaH}_2\text{PO}_2$

ii. Basic buffer: These are solutions of a mixture of weak base (W_B) and a salt of weak base with a strong acid (W_B/S_A)

For example:

- $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
- $\text{NH}_4\text{OH} + \text{NH}_4\text{NO}_3$
- $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4$
- $\text{NH}_4\text{OH} + \text{NH}_4\text{ClO}_4$
- $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{NH}_3^+\text{Cl}^\ominus$
- $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{NH}_3^+\text{HSO}_4^\ominus$
- $\text{PhNH}_2 + \text{PhNH}_3^+\text{Cl}^\ominus$





Note: Buffer solutions are actually conjugate acid-base pairs

ILLUSTRATION 8.48

Which of the following combinations of solute would result in the formation of a buffer solution?

a. $\text{CH}_3\text{COOH} + \text{NaOH}$ in

- 1:1 mol ratio
- 2:1 mol ratio
- 1:2 mol ratio

b. $\text{NH}_4\text{Cl} + \text{NH}_3$ in

- 1:1 mol ratio
- 2:1 mol ratio
- 1:2 mol ratio

c. $\text{HCl} + \text{NaCl}$

d. $\text{HCl} + \text{CH}_3\text{COOH}$

e. $\text{NaOH} + \text{HCl}$

a. (ii)

i. It will form salt of weak acid and strong base (W_A/S_B) CH_3COONa .

ii. It will form acidic buffer, since 1 mol of weak acid will be left unreacted and 1 mol of CH_3COONa will be formed.

iii. 1 mol of CH_3COONa and 1 mol of NaOH is left.

b. (i), (ii), (iii)

(i), (ii), and (iii) all are basic buffers since in all cases it is a mixture of salt of W_B/S_A (NH_4Cl) and W_B (NH_3).

Moreover, NH_4Cl and NH_3 do not react.

c. It is **not buffer** since it is a mixture of S_A (HCl) and salt of S_A/S_B (NaCl).

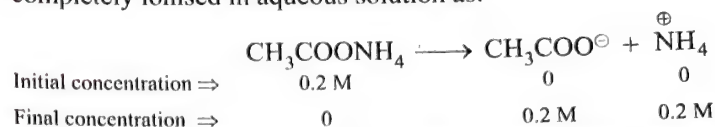
d. It is **not buffer** since it is a mixture of S_A (HCl) and W_A (CH_3COOH).

e. It is **not buffer** since it is a mixture of S_A (HCl) and S_B (NaOH).

8.11.2 BUFFER ACTION

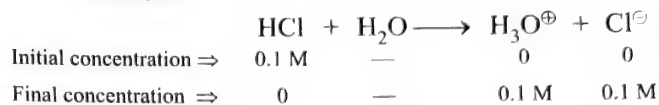
The property of a buffer solution to resist any change in its pH value even when small amount of the S_A or S_B is added to it is called 'Buffer action'.

Buffer action of ammonium acetate: Let 0.2 M of $\text{CH}_3\text{COONH}_4$ is taken. $\text{CH}_3\text{COONH}_4$ like other salts is almost completely ionised in aqueous solution as:

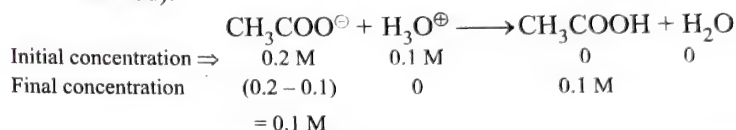


a. **When small amount of S_A is added to the buffer solution:**

Let a few drops of 0.1 M HCl is added to the above buffer solution.



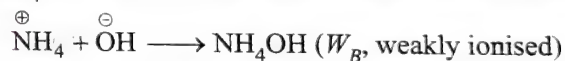
0.1 M of H_3O^+ given by HCl combines with 0.1 M CH_3COO^- ion to form 0.1 M CH_3COOH (W_A) (weakly ionised).



Thus, the formation of 0.1 W_A (CH_3COOH) does not change the pH effectively. Moreover, the concentration of H_3O^+ of the solution does not change practically and hence the pH of solution remains almost constant.

b. **When small amount of S_B is added to the buffer solution:**

Let a few drops of 0.1 M NaOH be added to the above buffer solution. The OH^- ions given by S_B (NaOH) combines with NH_4^+ ions to form weakly ionised molecule of NH_4OH .



Thus, the OH^- ion concentration and hence the H_3O^+ ion concentration or the pH of the solution remains almost constant.

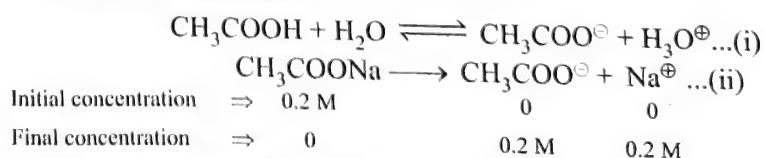
c. **Solution of NaCl (Salt of S_A/S_B) does not act as buffer:**

Since NaCl ionises completely to give Na^+ and Cl^- ions which combine with the S_A or S_B added to form HCl or

NaOH . But these ionise completely to give back OH^- or H_3O^+ ions. Thus, the H_3O^+ ions concentration of the solution changes and hence pH of the solution changes.

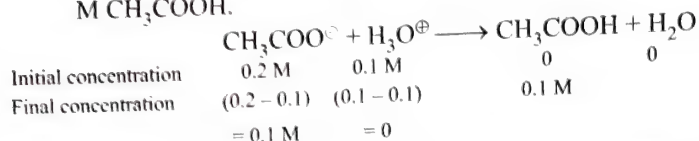
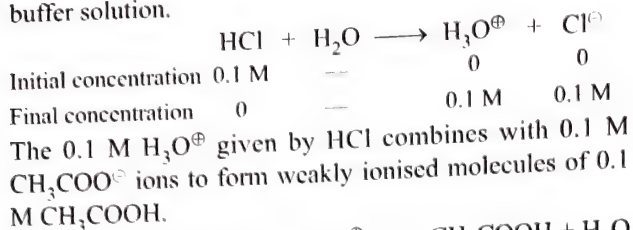
8.11.3 BUFFER ACTION OF ACIDIC BUFFER

Let us consider the buffer action of the acidic buffer containing 0.2 M CH_3COOH and 0.2 M CH_3COONa , CH_3COOH ionises to a small extent whereas CH_3COONa is almost completely ionised in the aqueous solution as:



Due to the **common ion effect**, the ionisation of CH_3COOH is further suppressed. Thus, in the solution, there are excess of CH_3COO^- ions and small amount of H_3O^+ ions.

- a. When small amount of S_A is added to the acidic buffer solution: Let a few drops of 0.1 M HCl be added to the above buffer solution.



Thus, the $[\text{H}_3\text{O}^{\oplus}]$ and hence the pH of the solution remains almost constant. Moreover, formation of 0.1 M CH_3COOH (W_A) does not change the pH of the solution effectively.

It is evident from the above reaction that on addition of 0.1 M HCl (S_A) to the acidic buffer the concentration of W_A (CH_3COOH) increases (0.2 + 0.1 = 0.3 M), whereas the concentration of CH_3COONa (salt of W_A/S_B) decreases (0.2 - 0.1 = 0.1 M)

Rule:AAA (for memorising)

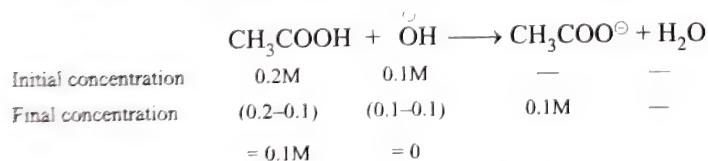
AAA rule is useful in solving problems based on buffer solution. It is stated as:

In acidic buffer (A), when strong acid (A) is added, the concentration of W_A (A) increases and concentration of salt (W_A/S_B) decreases.

Note: pH of the solution does not change due to the formation of weak acid (CH_3COOH).

- b. When small amount of S_B is added to the acidic buffer solution: Let a few drops of 0.1 M NaOH be added to the

above buffer solution. The 0.1 M OH^{\ominus} ions given by the NaOH combine with 0.1 M CH_3COOH already present to form 0.1 M $\text{CH}_3\text{COO}^{\ominus}$ ion.



Since the formation of 0.1 $\text{CH}_3\text{COO}^{\ominus}$ ion does not affect in the change of $[\text{H}_3\text{O}^{\oplus}]$ and hence pH does not change.

It is evident from the above reaction, that on addition of 0.1 M NaOH (S_B) in the acidic buffer the concentration of W_A (CH_3COOH) decreases (0.2 - 0.1 = 0.1 M) whereas the concentration of CH_3COONa (salt of W_A/S_B) increases (0.2 + 0.1 = 0.3 M)

Rule:ABA (for memorisation)

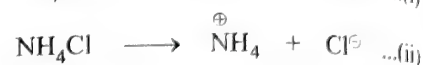
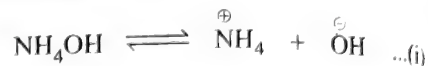
In acidic buffer (A), when strong base (B) is added, the concentration of weak acid (A) decreases and the concentration of salt (W_A/S_B) increases.

Note: pH of the solution does not change due to the formation of ($\text{CH}_3\text{COO}^{\ominus}$) salt of W_A and S_B .

8.11.4 BUFFER ACTION OF BASIC BUFFER

The buffer action of a basic buffer containing 0.2 M NH_4OH and 0.2 M NH_4Cl is explained as:

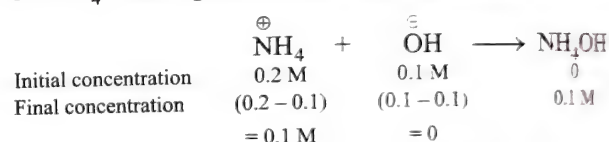
NH_4OH dissociates to small extent whereas NH_4Cl dissociates completely in aqueous solution as



Due to the common ion effect, the ionisation of NH_4OH is further suppressed. Thus, in the solution there are excess of NH_4^{\oplus} ions and small amount of OH^{\ominus} ions.

- a. When small amount of S_B is added to the basic buffer solution: Let a few drops of 0.1 M NaOH be added to the

above buffer solution. The 0.1 M OH^{\ominus} ions combine with 0.1 M NH_4^{\oplus} ions to give 0.1 M NH_4OH (weakly dissociated)



Due to the formation of weakly ionised NH_4OH , pH of the solution does not change effectively. Moreover, the $[\text{H}_3\text{O}^{\oplus}]$ is not changed, so the pH of the solution remains unaffected.

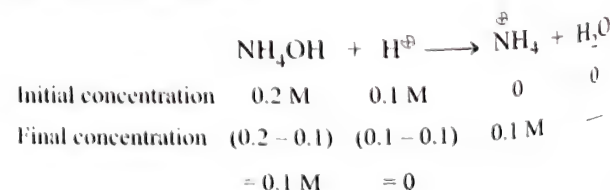
It is evident from the above reaction, that on addition of 0.1 M NaOH (S_B) to the basic buffer, the concentration of W_B (NH_4OH) increases (0.2 + 0.1 = 0.3 M), whereas the concentration of NH_4Cl (salt of W_B/S_A) decreases (0.2 - 0.1 = 0.1 M)

Rule: BBB (for memorisation)

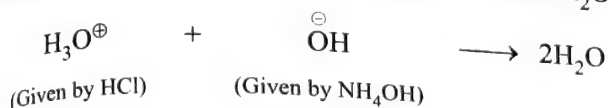
In basic buffer (B), when strong base (B) is added, the concentration of weak base (B) increases and the concentration of salt (W_B/S_A) decreases.

Note: pH of the solution does not change due to the formation of weak base (NH_4OH)

- b. When small amount of S_A is added to the basic buffer solution: Let a few drops of 0.1 M HCl be added to the above buffer solution. The 0.1 M H^{\oplus} combines 0.1 M NH_4OH to give 0.1 M NH_4^{\oplus} ions.



Due to the formation of NH_4^+ ions, pH of the solution does not change. Alternatively, $0.1 \text{ M H}_3\text{O}^+$ given by HCl, combines with 0.1 M OH^- (from NH_4OH) to form H_2O .



As the OH^- ions are consumed, the equilibrium (i) shifts in the forward direction. Thus more of NH_4OH dissociate to produce more of OH^- ions which make up the loss of OH^- ions. Hence the $[\text{OH}^-]$ and therefore, $[\text{H}_3\text{O}^+]$ or the pH of the solution remains fairly constant.

It is evident from the above reaction, that on addition of 0.1 M HCl (S_A) to the basic buffer, the concentration of W_B (NH_4OH) decreases ($0.2 - 0.1 = 0.1 \text{ M}$) whereas the concentration of NH_4Cl (salt of W_B/S_A) increases ($0.2 + 0.1 = 0.3 \text{ M}$).

Rule: BAB: (for memorisation)

In basic buffer (B), when strong acid (A) is added, the concentration of weak base (B) decreases and the concentration of salt (W_B/S_A) increases.

Note: pH of the solution does not change due to the formation of NH_4^+ ions (salt of W_B and S_A).

8.11.5 BUFFER ACTION OF A STRONG ACID (~0.1 M) AND A STRONG BASE (~0.1 M)

A solution of strong acid (e.g., HCl) of reasonable concentration (~0.1 M) acts as a buffer (See Fig. 8.7). The acid is completely dissociated and all the H^+ ions are present in the free form. Initial pH increases only by 0.3 even after half of the acid is neutralised, i.e. its concentration is reduced to less than 0.05. Same is true for a strong base whose solution acts as a buffer at higher pH (see later parts of the titration curves in Fig. 8.7 and 8.8) which now correspond to dilute solutions of NaOH in presence of same salt. It can be seen in Fig. 8.7 to 8.9 that some portions of the titration curves are flat, i.e., pH of titration mixtures changes very little even on addition of acid or base. It can be seen that these portions are generally mixtures of acid and salt or base and salt.

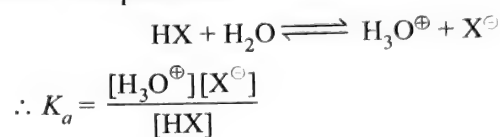
8.11.6 APPLICATIONS OF BUFFER SOLUTIONS

- Many body fluids, e.g., blood or urine have definite pH and any changes in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biological processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH.
- Acidic or basic buffer find enormous use in industrial processes and also in biological reactions. Like the pH of normal blood is 7.4, and for good health and even for the survival, it should not change below 7.1 or greater than 7.7. The body maintains the pH through a buffer system made of

CO_3^{2-} and HCO_3^- ions and H_2PO_4^- and HPO_4^{2-} . Similarly, the pH of gastric juice is kept constant in order to operate good digestive functions.

8.11.7 CALCULATION OF PH OF ACIDIC BUFFER SOLUTION OF ($\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$) (HENDERSON-HASSELBALCH EQUATION)

If weak acid is represented as HX, and its ionisation constant is given in the equation as:



$$\therefore [\text{H}_3\text{O}^+] = \frac{K_a [\text{HX}]}{[\text{X}^-]}$$

Taking negative logarithm on both sides, we get
 $-\log[\text{H}_3\text{O}^+] = -\log K_a - \log[\text{HX}] + \log[\text{X}^-]$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

The quantity $\frac{[\text{X}^-]}{[\text{HX}]}$ is the ratio of concentration of salt (or conjugate base of acid) and acid present in the mixture.

$$\text{Therefore, pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots(\text{i})$$

$$\text{pH} = 4.76 + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots(\text{ii})$$

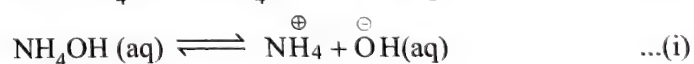
($\text{p}K_a$ of $\text{CH}_3\text{COOH} = 4.76$)

Equation (i) is known as Henderson-Hasselbalch equation.

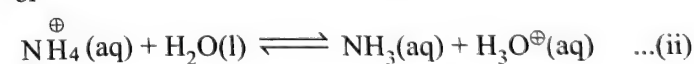
Note: A mixture of CH_3COOH and CH_3COONa acts as buffer solution around $\text{pH} = 4.75$.

8.11.8 CALCULATION OF PH OF BASIC BUFFER SOLUTION OF ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$)

Mixture of NH_4Cl and NH_4OH can be expressed in two ways:



or



or



$$\text{From equation (i), } K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

Taking negative logarithm on both sides, we get

$$-\log[\text{OH}^-] = -\log K_b - \log[\text{NH}_4\text{OH}] + \log[\text{NH}_4^+]$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

The quantity $\frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$ is the ratio of concentration of salt (or conjugate acid of base) and base present in the mixture.

$$\text{Therefore, } \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots(\text{iv})$$

$$\text{(or)} \quad 14 - \text{pOH} = 14 - \left[\text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \right]$$

$$\therefore \text{pH} = (14 - \text{p}K_b) - \log \left(\frac{[\text{Salt}]}{[\text{Base}]} \right)$$

$$\text{Since } \text{p}K_a + \text{p}K_b = 14$$

$$\text{pH} = \text{p}K_a - \log \frac{[\text{Salt}]}{[\text{Base}]} \quad (\text{p}K_a \text{ of } \text{NH}_4^+ = 9.25)$$

$$\text{pH} = 9.25 + \log \frac{[\text{Base}]}{[\text{Salt}]}$$

It is to be noted that the highest buffer capacity should be around 9.25 (When $[\text{Base}] = [\text{Salt}]$), and furthermore the concentration of NH_3 is actually the concentration of NH_4OH .

Note: A mixture of NH_4OH and NH_4Cl acts as buffer solution around $\text{pH} = 9.25$.

8.11.9 CHANGE IN pH OF AN ACIDIC BUFFER (WHEN AN ACID OR A BASE IS ADDED)

The addition of H^+ ions or OH^- ions to an acidic buffer (HA/A^-) does not appreciably change the pH of buffer. Similarly, we can analyse the same for a basic buffer (BOH/B^+).

In actual, pH of a buffer solution changes by a small quantity. Let us calculate this change in pH quantitatively.

Consider an acidic buffer HA/A^- , where $[\text{salt}] = [\text{A}^-]$ and $[\text{acid}] = [\text{HA}]$

- a. An acidic buffer is rich in A^- ions. Let us add x mol L^{-1} of HCl to it. This added HCl (H^+) reacts with A^- (salt) to give undissociated acid as follows:



Now using Henderson's equation,

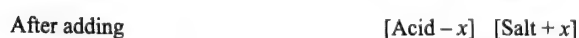
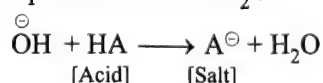
$$\text{pH(Original buffer)} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH(New)} = \text{p}K_a + \log \frac{[\text{Salt} - x]}{[\text{Acid} + x]} \quad (\text{using AAA rule})$$

\Rightarrow pH of buffer decreases.

Change or difference in $\text{pH} = \text{pH}(\text{New}) - \text{pH}(\text{Original})$

- b. Let us add x M NaOH to the buffer. This added NaOH (OH^- ions) reacts with acid (HA) to produce salt and H_2O .



$$\Rightarrow \text{pH}(\text{new}) = \text{p}K_a + \log \frac{[\text{Salt} + x]}{[\text{Acid} - x]} \quad (\text{using ABA rule})$$

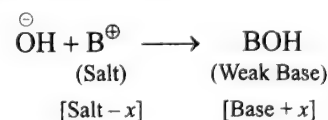
\Rightarrow pH of buffer increases.

Change in $\text{pH} = \text{pH}(\text{New}) - \text{pH}(\text{Original})$

8.11.10 CHANGE IN pH OF A BASIC BUFFER (WHEN AN ACID OR BASE IS ADDED)

Consider an basic buffer BOH/B^+ , where $[\text{salt}] = [\text{B}^+]$ and $[\text{weak base}] = [\text{BOH}]$.

- a. A basic buffer is rich in B^+ ions. Let us add x M NaOH to it. This added NaOH (OH^-) reacts with B^+ (salt) to give undissociated base as follows:



After adding x M OH^- ions:

Now using Henderson's equation

$$\text{pOH (original buffer)} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pOH}(\text{new}) = \text{p}K_b + \log \frac{[\text{Salt} - x]}{[\text{Base} + x]} \quad (\text{Using BBB rule})$$

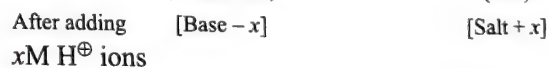
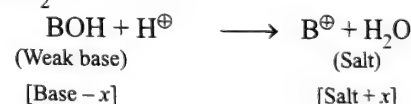
\Rightarrow pOH of buffer decreases.

\Rightarrow pH of buffer increases.

Change in $\text{pOH} = \text{pOH}(\text{New}) - \text{pOH}(\text{Original})$

Change in $\text{pH} = 14 - \text{Change in pOH}$.

- ii. Let us add x M HCl to the buffer. This added HCl (H^+ ions) reacts with BOH (weak base) to produce B^+ (Salt) and H_2O .



$$\therefore \text{pH (original buffer)} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\Rightarrow \text{pOH (new)} = \text{p}K_b + \log \frac{[\text{Salt} + x]}{[\text{Base} - x]} \quad (\text{Using BAB rule})$$

\Rightarrow pOH of buffer increases but pH decreases.

Change in $\text{pOH} = \text{pOH}(\text{New}) - \text{pOH}(\text{Original})$

Change in $\text{pH} = 14 - \text{Change in pOH}$.

Note: A buffer solution is assumed to be destroyed if on adding strong acid or base, its pH changes by ± 1 units (i.e., 2 units).

$\text{pH}(\text{new}) = \text{p}K_a \pm 1$ (if the initial pH of buffer solution was $\text{p}K_a$). This means the ratio $\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\frac{[\text{Salt}]}{[\text{Base}]} = 10$ or $\frac{1}{10}$.

8.11.11 BUFFER CAPACITY (β)

It is defined as the number of moles of acid or base that causes the change in pH of a litre of a buffer by 1 unit. Buffer capacity is a quantitative measure of the resistance of a buffer solution to acid or base.

$$\beta = \frac{dn}{d(\text{pH})} = 2.303 \left(\frac{K_w}{[\text{H}^+]} + [\text{H}^+] + \frac{C_{\text{Buffer}} K_a [\text{H}^+]}{(K_a + [\text{H}^+])^2} \right)$$

[Learn this formula as a direct result]

where dn is the infinitesimally small number of moles of acid or base added; $d(\text{pH})$ is the resulting change in pH;

$$C_{\text{Buffer}} = [\text{HA}] + [\text{A}^-] = \text{Total buffer concentration.}$$

However, for most of the buffer solutions, first and second terms in the above expression are relatively smaller as compared to the third term and hence the buffer capacity can be approximately defined as:

$$\beta = \frac{dn}{d(\text{pH})} = 2.303 \frac{C_{\text{Buffer}} K_a [\text{H}^+]}{(K_a + [\text{H}^+])^2}$$

Buffer capacity is also known as buffer efficiency, buffer index, or buffer value.

Buffer capacity of a buffer is maximum when $\text{pH} = \text{p}K_a$ and is given by:

$$\beta_{\text{Max}} = 2.303 \frac{C_{\text{Buffer}}}{4} \left[\because \frac{K_w}{K_a} \text{ and } K_a \text{ is small} \right]$$

Buffer capacity of a solution of a strong acid or base at any pH is given by:

$$\beta = \frac{dn}{d(\text{pH})} = 2.303 \{ [\text{OH}^-] + [\text{H}^+] \}$$

It has been seen experimentally that a solution of a strong acid has a high buffer capacity below a pH of 2. Likewise, a solution of a strong base has a high buffer capacity above the pH of 12.

Note: Buffer capacity as defined above is instantaneous and thus can be calculated at any instant. However, we can also define an average buffer capacity as:

$$\beta_{\text{Avg}} = \frac{\Delta n}{\Delta(\text{pH})}$$

For example: Calculate the buffer capacity of an HCl solution having a pH = 2.

$$\begin{aligned} \text{Sol. Buffer capacity} = \beta &= 2.303 \{ [\text{H}^+] + [\text{OH}^-] \} \\ &= 2.303 (10^{-2} + 10^{-12}) \\ &= 0.023. \end{aligned}$$

ILLUSTRATION 8.49

Calculate the pH of solution in which 0.2 M NH_4Cl and 0.1 M NH_3 are present the $\text{p}K_b$ of NH_3 solution is 4.75.

Sol. First Method:

The solution of NH_4Cl and NH_3 is a basic buffer solution. So applying buffer equation

$$\begin{aligned} \text{pOH} &= \text{p}K_b + \log \left[\frac{\text{Salt}}{\text{base}} \right] \\ &= 4.75 + \log \left(\frac{0.2}{0.1} \right) \end{aligned}$$

$$= 4.75 + \log 2$$

$$= 4.75 + 0.30$$

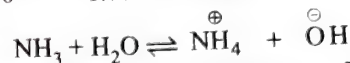
$$= 5.05$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 5.05 = 8.95$$

Second Method: The ionisation constant (k_b) of NH_3

$$k_b = \text{antilog} (-\text{p}K_b) \text{ i.e.}$$

$$k_b = 10^{-4.75} = 1.77 \times 10^{-5} \text{ M}$$



$$\text{Initial conc. (M)} \quad 0.1 \text{ M} \quad - \quad 0.20 \text{ M} \quad 0$$

$$\text{At equilibrium (M)} \quad (0.1 - x) \quad (0.20 + x) \quad x$$

$$k_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$= \frac{(0.20 + x)(x)}{(0.1 - x)} = 1.77 \times 10^{-5}$$

As k_b is small, neglect x in comparison to 0.1 M and 0.2 M thus,

$$\text{OH}^- = x = 0.88 \times 10^{-5}$$

$$\text{Therefore, } [\text{H}^+] = 1.12 \times 10^{-9}$$

$$\text{pH} = -\log[\text{H}^+] = 8.95$$

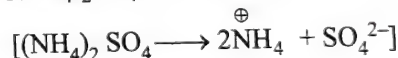
ILLUSTRATION 8.50

Calculate the pH of a solution made by mixing 0.1 M NH_3 and 0.1 M $(\text{NH}_4)_2\text{SO}_4$. ($\text{p}K_b$ of $\text{NH}_3 = 4.76$)

Sol. It is a basic buffer.

$$[\text{Base}] = [\text{NH}_3] = 0.1 \text{ M}$$

$$[\text{Salt}] = [(\text{NH}_4)_2\text{SO}_4] = 0.1 \times 2 = 0.2 \text{ M}$$



$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= 4.76 + \log \frac{0.2 \text{ M}}{0.1 \text{ M}}$$

$$= 4.76 + \log 2$$

$$= 4.76 + 0.3 = 5.06$$

$$\therefore \text{pH} = 14 - 5.03 = 8.94$$

ILLUSTRATION 8.51

How much volume of 0.1 M CH_3COOH should be added to 50 mL of 0.2 M NaAc solution to have a pH 4.91?

Sol. It is an acidic buffer

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.91 = 4.76 + \log \left[\frac{\text{Salt}}{\text{Acid}} \right]$$

$$\therefore \log \left[\frac{\text{Salt}}{\text{Acid}} \right] = (4.91 - 4.76) = 0.15$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \text{Antilog} (0.15) = 1.41$$

$$\text{mmoles of NaAc} = 50 \times 0.2 = 10$$

$$\text{mmoles of HAc required} = 0.1 \text{ M} \times V$$

$$\left[\frac{\text{Salt}}{\text{Acid}} \right] = 1.41 = \frac{10}{0.1 \times V}$$

$$\Rightarrow V = \frac{10}{0.1 \times 1.41} = 70.92 \text{ mL}$$

\therefore Volume of 0.1 M HAc required = 70.92 mL

ILLUSTRATION 8.52

- At what pH will the mixture of HCOOH and HCOONa give buffer solution of higher capacity?
- Calculate the ratio of $\frac{[\text{HCOONa}]}{[\text{HCOOH}]}$ in a buffer of pH 4.25. (K_a of HCOOH = 1.8×10^{-4})

Sol. i. Buffer capacity = $\frac{dpH}{dn \text{ acid or base}}$

Buffer capacity is the highest or maximum near the pK_a of acid (provided total number of moles of salt and acid remain constant). In this case,
 $pK_a = -\log(1.8 \times 10^{-4}) = 3.74$.

This is the pH of high capacity buffer.

- In order to obtain a buffer solution of pH = 4.25, according to Henderson's equation,

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.25 = 3.74 + \log \left[\frac{\text{Salt}}{\text{Acid}} \right]$$

$$\left[\frac{\text{Salt}}{\text{Acid}} \right] = \text{antilog}(4.25 - 3.74) \\ = \text{antilog}(0.51) = 3.24$$

ILLUSTRATION 8.53

How much of 0.3 M NH_4OH should be mixed with 30 mL of 0.2 M solution of NH_4Cl to give buffer solution of pH 8.65?

Sol. It is a basic buffer.

$$\text{i. } pH = 8.65, pOH = 14 - 8.65 = 5.35$$

$$pOH = pK_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$5.35 = 4.75 + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \text{antilog}(5.35 - 4.75) \\ = \text{antilog}(0.6) \approx 4.0$$

$$\therefore \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{30 \times 0.2}{0.3 \times V} \approx 4.0$$

$$\therefore V = 5 \text{ mL}$$

ILLUSTRATION 8.54

Calculate the pH of the following mix-tures given $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$ ($pK_a = pK_b = 4.7447$).

a. 50 mL 0.05 M NaOH + 50 mL of 0.1 M CH_3COOH

b. 50 mL 0.1 M NH_4OH + 50 mL of 0.05 M HCl

Sol. a. $[\text{NaOH}] = 2.5 \text{ mmol}$; $[\text{HAc}] = 5 \text{ m mols}$; $[\text{CH}_3\text{COOH}]_{\text{left}} = 2.5 \text{ mmol}$; $[\text{salt}] \text{ formed} = 2.5 \text{ mmol}$
 $pH = pK_a + \log(\text{salt/acid}) = 4.7447 + \log(2.5/2.5) = 4.7447$

b. $[\text{NH}_4\text{OH}] = 5 \text{ mmol}$, $[\text{HCl}] = 2.5 \text{ mmol}$
 $[\text{NH}_4\text{OH}]_{\text{left}} = 2.5 \text{ mmol}$
 $[\text{NH}_4\text{Cl}] \text{ formed} = 2.5 \text{ mmol}$
 $pOH = pK_b + \log(\text{salt/base}) = 4.7447 + \log(2.5/2.5) = 4.7447$
 $pH = 14 - 4.7447 = 9.2553$

ILLUSTRATION 8.55

What volume of strong monobasic acid of normality 10 is needed to prepare 1 L of a buffer solution of pH 9, using 1 mol of NH_3 and as much of strong acid needed. (K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$) ($pK_b = 4.7447$)

Sol. NH_4Cl is a salt of S_A/W_B

[Since $W_B(\text{NH}_3)$ is left and NH_4Cl is formed. So, a mixture of W_B and salt is formed, which is a basic buffer]



Initial 1 x

Final (1 - x) x

$$pOH = 14 - 9 = 5$$

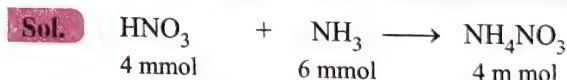
$$pOH = pK_b + \log(\text{salt/base})$$

$$5 = 4.7447 + \log(x/1 - x) \text{ and } x = 0.64.$$

$$N_1 V_1 = 0.64 \text{ and } V_1 = 0.64/10 = 0.064 \text{ L} = 64 \text{ mL}$$

ILLUSTRATION 8.56

40 mL sample of 0.1 M solution of nitric acid is added to 20 mL of 0.3 M aqueous ammonia. What is the pH of the resulting solution? ($pK_b = 4.7447$)



[Since $W_B(\text{NH}_3)$ is left and salt (NH_4NO_3) is formed so it is a basic buffer]

$$\text{Base left} = 6 - 4 = 2 \text{ mmol}$$

$$[\text{Acid}] = 40 \times 0.1 = 4 \text{ mmol}$$

$$[\text{Base}] = 20 \times 0.3 = 6 \text{ mmol}$$

$$\therefore pOH = 4.7447 + \log 4/2 = 5.0457 \text{ and}$$

$$pH = 14 - 5.0457 = 8.95$$

ILLUSTRATION 8.57

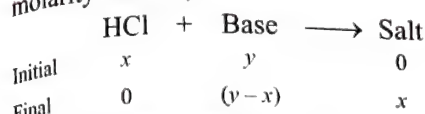
The base imidazole has a K_b of 8.1×10^{-8} .

a. In what amounts should 0.02 M HCl and 0.02 M imidazole be mixed to make 100 mL of a buffer at pH 7?

b. If the resulting solution is diluted to 1 L, what is the pH of the diluted solution?

Sol. a. $pOH = pK_b + \log(\text{salt/base})$
 $7 = 8 - 0.90848 + \log(\text{salt/base})$ and
 $(\text{base/salt}) = 1.23458$.

Let x mL of HCl and y mL of imidazole are mixed (since molarity is same)



$$x + y = 100 \text{ mL}, y = 100 - x$$

$$\frac{\text{Base}}{\text{Salt}} = \frac{y-x}{x} = \frac{100-2x}{x} = 1.23458$$

$$x = 30.9 \text{ mL (volume of acid)}$$

$$\text{Volume of imidazole} = 100 - 30.9 = 69.1$$

- b. pH remains same (since on dilution the concentration of salt and base changes in the same proportions).

ILLUSTRATION 8.58

In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10 mL of NaOH solution has been added and 6.40 after 20 mL of the NaOH has been added. What is the ionisation constant of the acid HX?

Sol. Let the normality of HX and NaOH = 1.

Let x mEq or mmol of HX is present initially.

When pH = 5.8

$$[\text{Salt}] = 10 \times 1 = 10 \text{ mmol}$$

$$[\text{Acid}] = (x - 10) \text{ mmol}$$

When pH = 6.4

$$[\text{Salt}] = 20 \times 1 = 20 \text{ mmol}$$

$$[\text{Acid}] = (x - 20) \text{ mmol}$$

$$5.8 = \text{p}K_a + \log(10/x - 10) \quad \dots(i)$$

$$6.4 = \text{p}K_a + \log(20/x - 20) \quad \dots(ii)$$

Solving equations (i) and (ii), calculate the value of x and $\text{p}K_a$.

$$\therefore \text{p}K_a = 6.1$$

ILLUSTRATION 8.59

A definite volume of an aqueous N/20 acetic acid ($\text{p}K_a = 4.74$) is titrated with a strong base. It is found that 75 equal-sized drops of NaOH added from a burette effect the complete neutralisation. Find the pH when an acid solution is neutralised to the extent of 20%, 40%, and 90%, respectively.

Sol. During the titration of weak acid with strong base, if weak acid is left behind, acidic buffer is formed.

- i. 20% neutralisation of W_A means 20% salt of W_A/S_B is formed and 80% W_A is left.

$$\therefore \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.74 + \log \left(\frac{20}{80} \right)$$

$$= 4.74 + \log \left(\frac{1}{4} \right)$$

$$= 4.74 - \log 2^2$$

$$= 4.74 - 2 \times 0.3 = 4.14$$

- ii. 40% neutralisation of W_A means 40% salt of W_A/S_B is formed and 60% W_A is left.

$$\therefore \text{pH} = 4.74 + \log \left(\frac{40}{60} \right)$$

$$= 4.74 + \log 2 - \log 3$$

$$= 4.74 + 0.3 - 0.48 = 4.56$$

- iii. 90% neutralisation of W_A means 90% salt of W_A/S_B is formed and 10% W_A is left.

$$\therefore \text{pH} = 4.74 + \log \left(\frac{90}{10} \right)$$

$$= 4.74 + \log 3^2$$

$$= 4.74 + 2 \times 0.48 = 5.70$$

ILLUSTRATION 8.60

How many moles of NaOH can be added to 1.0 L of solution of 0.1 M NH_3 and 0.1 M NH_4Cl without changing pOH by more than one unit ($\text{p}K_b$ of $\text{NH}_3 = 4.75$)?

Sol. It is a basic buffer

$$\text{pOH} = \text{p}K_b + \log \left[\frac{\text{Salt}}{\text{base}} \right]$$

$$\text{pOH} = 4.75 + \log \left[\frac{0.1}{0.1} \right]$$

$$\text{pOH} = \text{p}K_b = 4.75.$$

Let x mol of NaOH is added (rule BBB). In a basic buffer (B), on adding strong base (B), the concentration of weak base (B) increases and that of salt decreases. On adding the base, pH will increase and pOH will decrease.

$$\text{New pOH} = 4.75 - 1 = 3.75$$

$$\therefore 3.75 = 4.75 + \log \left[\frac{0.1-x}{0.1+x} \right]$$

$$3.75 - 4.75 = \log \left[\frac{0.1-x}{0.1+x} \right]$$

$$-1 = \log \left[\frac{0.1-x}{0.1+x} \right]$$

Taking antilog both sides

$$\frac{1}{10} = \frac{0.1-x}{0.1+x}$$

$$0.1+x = 10(0.1-x)$$

$$= 1 - 10x$$

$$\therefore 11x = 1 - 0.1$$

$$11x = 0.9$$

$$x = \frac{0.9}{11} = 0.082 \text{ mol.}$$

$$x = 0.082 \text{ mol} = 0.082 \text{ M (V = 1 L)}$$

ILLUSTRATION 8.61

How many moles of HCl can be added to 1.0 L of solution of 0.1 M NH_3 and 0.1 M NH_4Cl without changing pOH by more than one unit? ($\text{p}K_b$ of $\text{NH}_3 = 4.75$)

Sol. Proceed as above in part (a). Rule (BAB). In basic buffer, (B), on adding a strong acid (A), the concentration of weak base (B) decreases and salt increases.

On adding the the strong acid, pH decreases and pOH increases.

$$\text{New pOH} = 4.75 + 1 = 5.75.$$

$$\therefore 5.75 = 4.75 + \log \left[\frac{0.1+x}{0.1-x} \right]$$

$$5.75 - 4.75 = \log \left[\frac{0.1+x}{0.1-x} \right]$$

$$1 = \log \left[\frac{0.1+x}{0.1-x} \right]$$

Taking antilog both sides

$$10 = \frac{0.1+x}{0.1-x}$$

$$1 - 10x = 0.1 + x$$

$$11x = 0.9 \Rightarrow x = \frac{0.9}{11} = 0.082 \text{ mol.}$$

$$x = 0.082 \text{ mol} = 0.082 \text{ M } (V = 1 \text{ L})$$

ILLUSTRATION 8.62

A buffer solution of pH value 4 is to be prepared, using CH_3COOH and CH_3COONa . How much amount of sodium acetate is to be added to 1.0 L of M/10 acetic acid? ($K_a = 2.0 \times 10^{-5}$)

Sol. For an acidic buffer containing acetic acid, CH_3COOH , and sodium acetate, CH_3COONa , we have

$$[\text{H}^+] = \frac{K_a [\text{acid}]}{[\text{salt}]}$$

$$(\text{Use this formula, rather than}) \text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$[\text{CH}_3\text{COOH}] = 0.1 \text{ M};$$

$$[\text{H}^+] = 10^{-4} \text{ M and let } [\text{CH}_3\text{COONa}] = x \text{ M}$$

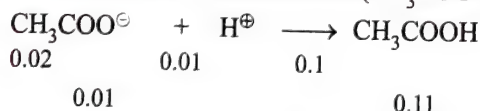
$$\Rightarrow [\text{H}^+] = 10^{-4} = \frac{2 \times 10^{-5} \times 0.1}{x}$$

$$\Rightarrow x = 0.02 \text{ mol, i.e. } 0.02 \text{ mol of } \text{CH}_3\text{COONa} \text{ is required.}$$

ILLUSTRATION 8.63

What will be the pH if 0.01 mol of HCl is dissolved in the above buffer solution? Find the change in pH value.

Sol. Now 0.01 mol of HCl ($[\text{H}^+] = 0.01 \text{ M}$) is added to 1 L of buffer, this will react with acetate ion (CH_3COO^-) as:



$$\Rightarrow [\text{acid}] = 0.11 \text{ M and } [\text{salt}] = 0.01 \text{ M } [V = 1.0 \text{ L}]$$

$$\Rightarrow \text{pH}_{\text{new}} = \text{p}K_a + \log \frac{0.01}{0.11}$$

$$= 4.7 + (-1.04) = 3.66 \text{ [use } \log 11 = 1.04]$$

$$\Rightarrow \text{Change in pH} = 3.66 - 4.0 = -0.34$$

ILLUSTRATION 8.64

How will the pH be affected if 1.5 L of H_2O is added to the above buffer?

Sol. Now, if 1.5 L of H_2O is added, it just increases the volume, thereby decreasing concentrations of both acid and salt. The ratio $\log \frac{[\text{salt}]}{[\text{acid}]}$ remains constant. Hence, pH remains same.

ILLUSTRATION 8.65

Calculate the pH of a buffer by mixing 0.15 mole of NH_4OH and 0.25 mole of NH_4Cl in a 1000 mL solution K_b for $\text{NH}_4\text{OH} = 2.0 \times 10^{-5}$.

Sol. 0.15 mol of NH_4OH and 0.25 mol of NH_4Cl in 1000 mL (1.0 L) solution give a basic buffer.

$$\text{pH} = 14 - \text{pOH}$$

Now using Henderson's equation:

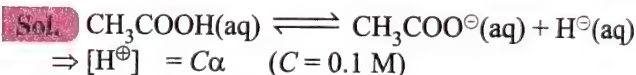
$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\Rightarrow \text{pOH} = -\log(2.0 \times 10^{-5}) + \log \left(\frac{0.25/1}{0.15/1} \right) = 4.92$$

$$\Rightarrow \text{pH} = 14 - 4.92 = 9.08$$

ILLUSTRATION 8.66

To 1.0 L of a decimolar solution of acetic acid, how much dry sodium acetate be added (in moles) so as to decrease the concentration of H^+ ion to 1/10th of its previous value? $K_a = 2.0 \times 10^{-5}$.



$$= \sqrt{K_a C} = \sqrt{2.0 \times 10^{-5} \times 0.1} = 1.41 \times 10^{-3} \text{ M}$$

[Check yourself that approximations are valid]

Note that when salt, CH_3COONa is added, the solution will behave just like an acidic buffer solution.

Using, Henderson's equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\Rightarrow [\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]} \text{ or } [\text{salt}] = K_a \frac{[\text{acid}]}{[\text{H}^+]}$$

$$\text{Now, } [\text{H}^+]_{\text{new}} = \frac{1}{10} \times 1.41 \times 10^{-3} \text{ M} = 1.41 \times 10^{-4} \text{ M}$$

$$\Rightarrow [\text{salt}] = \frac{(2.0 \times 10^{-5})(0.1)}{1.41 \times 10^{-4}} = 0.0142 \text{ M}$$

$$\Rightarrow \text{moles of salt, sodium acetate} = 0.0142 (\equiv 14.2 \text{ mmol}) \text{ per } 1.0 \text{ L is required. } (V = 1.0 \text{ L})$$

ILLUSTRATION 8.67

Calculate the pH of 0.10 M NH_3 solution Calculate the pH after 50 mL of this solution is treated with 25 mL of 0.10 M HCl.

$$(k_b \text{ of } \text{NH}_3 = 1.77 \times 10^{-5}, \text{p}k_b = 4.76)$$

Sol. First Method:

$$\text{mmoles of } \text{NH}_3 = 0.10 \text{ M} \times 50 \text{ mL} = 5$$

$$\text{m moles of HCl} = 0.10 \text{ M} \times 25 \text{ mL} = 2.5$$

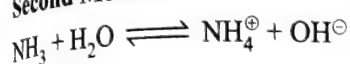
2.5 mmols of HCl react with 2.5 mmols of NH_3 to form 2.5 mmols of NH_4Cl and 2.5 mmols of NH_3 is left and forms a basic buffer solution.

	NH_3	+	HCl	\rightarrow	NH_4Cl
Initial mmols	5		2.5		2.5
Left (mmols)	$(5 - 2.5)$ $= 2.5$		0		2.5

$$\begin{aligned}\therefore \text{pOH} &= \text{p}k_b + \log \left[\frac{\text{Salt}}{\text{Base}} \right] \\ &= 4.76 + \log \left(\frac{2.5}{2.5} \right) \\ &= 4.76\end{aligned}$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.76 = 9.24$$

Second Method:



$$k_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.77 \times 10^{-5}$$

Before neutralisation

$$[\text{NH}_4^+] = [\text{OH}^-] = x$$

$$[\text{NH}_3] = 0.10 - x \approx 0.10$$

$$\therefore \frac{x^2}{0.10} = 1.77 \times 10^{-5}$$

$$\text{Thus } x = 1.33 \times 10^{-3} = [\text{OH}^-]$$

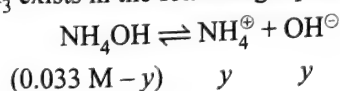
$$\begin{aligned}\text{Therefore, } [\text{H}^+] &= \frac{k_w}{[\text{OH}^-]} = \frac{10^{-14}}{(1.33 \times 10^{-3})} \\ &= 7.51 \times 10^{-12}\end{aligned}$$

$$\text{pH} = -\log (7.5 \times 10^{-12}) = 11.12$$

On addition of 25 mL of 0.1 M HCl solution (i.e. 2.5 mmol of HCl) to 50 mL of 0.1 M NH_3 solution (i.e., 5 mmol of NH_3), 2.5 mmol of NH_3 are neutralised. The resulting 75 mL (25 mL + 50 mL) solution contains the remaining unneutralised 2.5 mmol. of NH_3 and 2.5 mmol of NH_4^+ .

	NH_3	+	HCl	\rightleftharpoons	NH_4^+	+	Cl^-
[Initial at eq.]	2.5		2.5		0		0
[At eq.]	0		0		2.5		2.5

The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e. $2.5/75 = 0.033$ M) and 0.033 M of unneutralised NH_3 . This NH_3 exists in the following equilibrium:



$$\text{where } y = [\text{OH}^-] = [\text{NH}_4^+]$$

The final 75 mL solution after neutralisation already contains 0.033 M NH_4^+ ions, thus total concentration of NH_4^+ ions, is $[\text{NH}_4^+] = 0.033 + y$

$$\therefore k_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{(0.033)y}{(0.033)} = 1.77 \times 10^{-5} \text{ M}$$

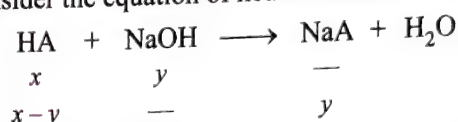
$$\begin{aligned}\text{Thus, } y &= 1.77 \times 10^{-5} = [\text{OH}^-] \\ [\text{H}^+] &= 10^{-14}/1.77 \times 10^{-5} = 0.56 \times 10^{-9} \\ \text{Hence } \text{pH} &= 9.24\end{aligned}$$

ILLUSTRATION 8.68

The equivalence point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.5 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid?

Sol. Let x mmol of HA is taken initially. Find x .

Consider the equation of neutralisation:



At equivalent point, millimoles of acid = millimoles of NaOH [i.e., $x = y$]

$$\Rightarrow \text{millimoles HA} = x = 3.5 \text{ [35 mL of 0.1 M NaOH]}$$

$$\text{At pH} = 5.5, \text{ mmol of NaOH added} = 2 = y$$

$$[20 \text{ mL of 0.1 M NaOH}]$$

$$\Rightarrow \text{mmol of HA left} = x - y = 1.5$$

$$\text{and mmol of NaA formed} = 2$$

Now such a solution will behave as an acidic buffer, whose pH is given as:

$$\begin{aligned}[\text{H}^+] &= \frac{K_a [\text{acid}]}{[\text{salt}]} \Rightarrow 10^{-5.5} = K_a \frac{1.5}{2} [10^{-5.5} = \sqrt{10} \times 10^{-6}] \\ \Rightarrow K_a &= 4.22 \times 10^{-6}\end{aligned}$$

ILLUSTRATION 8.69

Consider a buffer solution containing 0.1 mol each of acetic acid and sodium acetate in 1.0 L of solution, 0.01 mol of NaOH is gradually added to this buffer solution. Calculate the average buffer capacity of the solution and as well as initial and final buffer capacity. ($K_a = 2 \times 10^{-5}$, $\text{p}K_a = 4.7$)

Sol. pH of the solution is given by

$$\text{pH} = \text{p}K_{a_{\text{initial}}} + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}; \text{pH}_{\text{initial}} = 4.7$$

$$\text{when 0.01 M NaOH is added, } [\text{salt}] = 0.1 + 0.01 = 0.11 \text{ M}$$

$$\text{and } [\text{acid}] = 0.1 - 0.01 = 0.09 \text{ M}$$

\Rightarrow Final pH of solution:

$$\text{pH} = \text{p}K_a + \log \frac{0.11}{0.09} = 4.787$$

$$\Rightarrow [\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

$$= 2 \times 10^{-5} \times \frac{0.09}{0.11} = 1.64 \times 10^{-5} \text{ M}$$

$$\Delta(\text{pH}) = 4.787 - 4.7 = 0.087$$

$$\text{Thus, } \beta_{\text{Avg}} = \frac{\Delta n}{\Delta(\text{pH})} = \frac{0.01}{0.087} = 0.1148$$

$$C_{\text{Buffer}} = [\text{HA}] + [\text{A}^-] = 0.1 + 0.1 = 0.2 \text{ M}$$

$$\text{pH initial} = 4.7, [\text{H}^{\oplus}] \text{ initial} = 2 \times 10^{-5}, K_a = 2 \times 10^{-5}$$

$$\beta_{\text{Initial}} = 2.303 \frac{C_{\text{Buffer}} \cdot K_a [\text{H}^{\oplus}]}{[K_a + [\text{H}^{\oplus}]]^2}$$

$$\beta_{\text{Initial}} = 2.303 \frac{0.2 \times 2 \times 10^{-5} \times 2 \times 10^{-5}}{(2 \times 10^{-5} + 2 \times 10^{-5})^2} = 0.115$$

$$[\text{H}^{\oplus}]_{\text{Final}} = 1.64 \times 10^{-5} \text{ M.}$$

$$\beta_{\text{Final}} = 2.303 \frac{0.2 \times 2 \times 10^{-5} \times 1.64 \times 10^{-5}}{(2 \times 10^{-5} + 1.64 \times 10^{-5})^2} = 0.114$$

Note: Buffer capacity will decrease as more and more NaOH is added into the above solution. Check yourself that initially the buffer capacity was maximum. So, when 0.01 M NaOH was added, we will see a very slight decrease in the buffer capacity but as more and more NaOH is added, buffer capacity will decrease sharply and the difference between the average and maximum buffer capacity will get magnified.

If 0.05 M NaOH is added in the solution initially, we can calculate the final pH as:

$$\text{pH} = \text{p}K_a + \log \frac{0.15}{0.05} = 5.177$$

$$\text{Thus, } \beta_{\text{Avg.}} = \frac{\Delta n}{\Delta(\text{pH})} = \frac{0.05}{0.477} = 0.105$$

Calculate β_{Initial} and β_{Final} yourself.

8.12 HYDROLYSIS OF SALTS AND THE PH OF THEIR SOLUTIONS

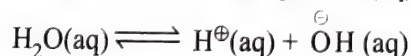
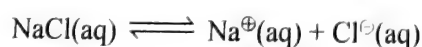
Salt hydrolysis describes the interaction of water and the cation/anion or both of a salt. The pH of the solution is affected by this interaction. The cations (e.g., Na^{\oplus} , Rb^{\oplus} , Ca^{2+} , Ba^{2+} , etc.) of the strong acids do not hydrolyse and therefore the solutions of salts formed by strong acids and strong bases are neutral, i.e. their pH is 7, whereas the solutions of salts formed by strong bases and weak acids are alkaline, i.e. their pH > 7. While the solutions of salts formed by strong acids and weak bases are acidic, i.e., pH < 7.

The phenomenon of interaction of cations and anions of the salts with H^{\oplus} and OH^{\ominus} ions furnished by water so that there is some net change in the pH of the resulting solution is known as *hydrolysis of a salt*.

Four cases have been discussed here to understand the behaviour of various type of salts.

8.12.1 SALTS OF STRONG ACIDS AND STRONG BASES S_A/S_B

When such salts are dissolved in water, they do not undergo hydrolysis. They simply ionise and fail to change the H^{\oplus} ion concentration of solution and hence the pH of the solution remains same, e.g., NaCl , CaCl_2 , BaCl_2 , KCl , NaNO_3 , Na_2SO_4 , and $\text{Ca}(\text{NO}_3)_2$.



The final pH of the solution remains 7 at 25°C.
(If NaOH and HCl are formed, they neutralise each other to keep the pH same).

8.12.2 SALTS OF WEAK ACIDS AND STRONG BASES W_A/S_B

Such salts give alkaline solutions in water. Some of such salts are: CH_3COONa , Na_2CO_3 , K_2CO_3 , and KCN . For our discussion, we consider CH_3COONa (sodium acetate) in water. When CH_3COONa is put in water, it completely ionises to give $\text{CH}_3\text{COO}^{\ominus}$ (acetate) ions and Na^{\oplus} ions.

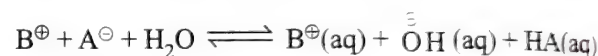
Now acetate ions ($\text{CH}_3\text{COO}^{\ominus}$) absorb some H^{\oplus} ions from weakly dissociated H_2O molecules to form undissociated CH_3COOH . Na^{\oplus} remains in ionic state in water.

Now for K_a (ionic product) of water to remain constant, H_2O further ionises to produce more H^{\oplus} and OH^{\ominus} ions. H^{\oplus} ions are taken up by $\text{CH}_3\text{COO}^{\ominus}$ ions leaving OH^{\ominus} ions in excess and hence an alkaline solution.

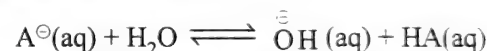
Let BA represents such a salt. As it is put in water:



BA dissociates into ions and BOH being strong base also ionises.



So, the net reaction is:



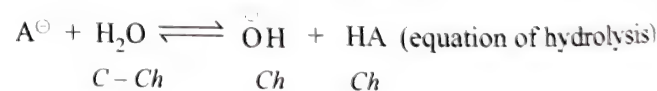
[It is also called anionic hydrolysis]

The above equation is known as the equation of hydrolysis and the equilibrium constant for such reactions is called as hydrolysis constant (K_h).

$$K_h = \frac{[\text{OH}^{\ominus}][\text{HA}]}{[\text{A}^{\ominus}]}$$

Degree of hydrolysis

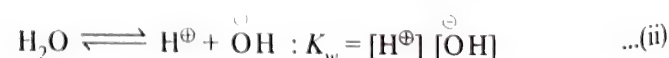
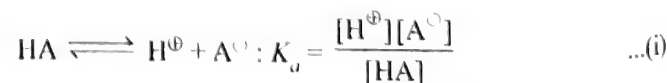
It is defined as the fraction of total salt that has undergone hydrolysis on attainment of equilibrium. It is denoted by h . Let c be the concentration of salt and h be its degree of hydrolysis.



$$K_h = \frac{[\text{OH}^{\ominus}][\text{HA}]}{[\text{A}^{\ominus}]} = \frac{(Ch)(Ch)}{C - Ch} = \frac{Ch^2}{1 - h}$$

$$\Rightarrow K_h = Ch^2 \quad [\text{assuming } h \ll 1] \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

Now considering dissociations of weak acid HA and H_2O .



$$\Rightarrow K_h = \frac{K_w}{K_a} \quad (\text{Subtracting equation (i) from equation (ii), we get the equation of hydrolysis})$$

Note: Weaker is the acid, greater is the hydrolysis constant.
The degree of hydrolysis increases when C decreases, i.e., with dilution.
Now substituting the value of K_h in expression of h .

$$\Rightarrow h = \sqrt{\frac{K_w}{K_a C}}$$

pH of solution

pH of a basic solution is given as

$$\text{pH} = 14 + \log [\text{OH}^-] \quad \text{and} \quad [\text{OH}^-] = Ch = \sqrt{K_h C}$$

Substituting for K_h , we get

$$[\text{OH}^-] = \sqrt{\frac{K_w C}{K_a}}$$

$$\Rightarrow \text{pH} = 14 + \log \sqrt{\frac{K_w C}{K_a}}$$

$$\Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

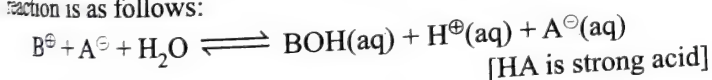
$$\text{or pH (at } 25^\circ\text{C)} = 7 + \frac{1}{2} (\text{p}K_a + \log C)$$

8.12.3 SALTS OF STRONG ACIDS AND WEAK BASES S_A/W_B

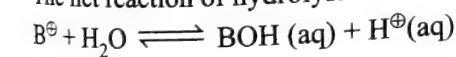
Such salts give acidic solutions in water. Some of such salts are: NH_4Cl , ZnCl_2 , and FeCl_3 . For the purpose of discussion, we will consider hydrolysis of NH_4Cl .

When NH_4Cl is put in water, it completely ionises in water to give NH_4^+ and Cl^- ions. NH_4^+ ions combine with OH^- ions furnished by weakly dissociated water to form NH_4OH (weak base). Now for keeping K_w constant, water further ionises to give H^+ and OH^- ions, where OH^- ions are consumed by NH_4^+ ions leaving behind H^+ ions in solution to give an acidic solution.

Let BA be one of such salts. When it is put into water, the reaction is as follows:



The net reaction of hydrolysis is:

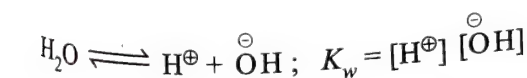
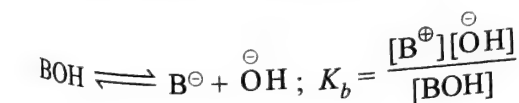


[It is also called cationic hydrolysis]

$$\Rightarrow K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]} = \frac{(Ch)(Ch)}{C - Ch} = \frac{Ch^2}{1 - h} = Ch^2$$

$$(h \ll 1) \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

Considering ionisation of weak base BOH and H_2O



From expressions for K_h , K_b , and K_w we have
(As in section 8.6.2)

$$K_h = \frac{K_w}{K_b} \Rightarrow h = \sqrt{\frac{K_w}{K_b C}}$$

pH of Solution

$$\text{Now, } \text{pH} = -\log [\text{H}^+]$$

$$\text{and } [\text{H}^+] = Ch = C \sqrt{\frac{K_h}{C}} = \sqrt{K_h C} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_w C}{K_b}}$$

$$\Rightarrow \text{pH} = -\log \sqrt{\frac{K_w C}{K_b}}$$

$$\Rightarrow \text{pH} = \log \sqrt{\frac{K_w C}{K_b}}$$

$$\Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$$

$$\text{or pH (at } 25^\circ\text{C)} = 7 - \frac{1}{2} (\text{p}K_b + \log C)$$

For example

- Calculate pH of M/100 solution of CH_3COONa at 25°C where K_a of CH_3COOH is 2.0×10^{-5} . ($\text{p}K_a = 4.7$)
- Calculate pH of M/100 solution of NH_4Cl at 25°C where K_b for NH_4OH is 2.0×10^{-5} . ($\text{p}K_b = 4.7$)
- In above two cases, find the degree of hydrolysis taking $K_w = 10^{-14}$.

Sol. a. It is a salt of W_A/S_B ($\text{p}K_a = 4.7$)

$$\therefore \text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$$

$$= \frac{1}{2} (14 + 4.7 + \log 10^{-2})$$

$$= 8.35 \quad (\text{pH} > 7, \text{ solution is basic})$$

b. It is a salt of W_B/S_A ($\text{p}K_b = 4.7$)

$$\therefore \text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$$

$$= \frac{1}{2} (14 - 4.7 - \log 10^{-2})$$

$$= 5.65 \quad (\text{pH} < 7, \text{ Solution is acidic})$$

$$\text{c. i. } h = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{10^{-14}}{2 \times 10^{-5} \times 10^{-2}}} = \sqrt{\frac{10^{-7}}{2}}$$

$$= \sqrt{\frac{10^{-8}}{20}} = 0.22 \times 10^{-4}$$

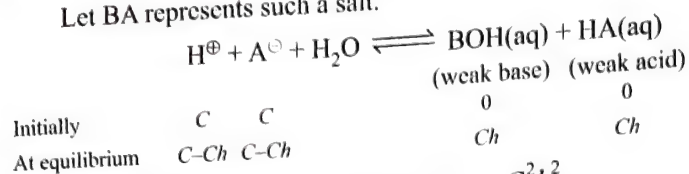
$$\text{ii. } h = \sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{10^{-14}}{2 \times 10^{-5} \times 10^{-2}}} = 0.22 \times 10^{-4}$$

8.12.4 SALTS OF WEAK ACIDS AND WEAK BASES W_A/W_B

Let us consider ammonium acetate ($\text{CH}_3\text{COONH}_4$) for our discussion. Both NH_4^+ ions and CH_3COO^- ions react, respectively,

with OH^- and H^+ ions furnished by water to form NH_4OH (weak base) and CH_3COOH (acetic acid).

Let BA represents such a salt.



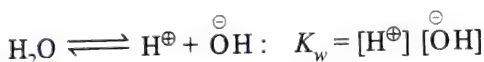
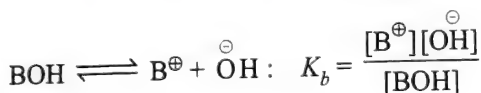
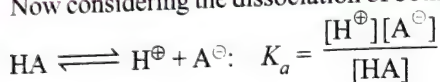
$$\Rightarrow K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = \frac{(\text{Ch})(\text{Ch})}{(\text{C}-\text{Ch})^2} = \frac{\text{C}^2 h^2}{\text{C}^2 (1-h)^2}$$

$$\Rightarrow K_h = \frac{h^2}{(1-h)^2}; \text{ taking square root on both sides to get:}$$

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}} \quad (\text{Here, } 1-h \neq 1)$$

Note: Hence, the degree of hydrolysis of such salts is independent of the concentration of salt solution.

Now considering the dissociation of both weak base and acid.



Combining K_h , K_b , K_a , and K_w , we have

$$K_h = \frac{K_w}{K_a K_b} \text{ and } h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

[It is also called cationic-anionic hydrolysis]

(Observe that $1-h \neq 1$) (if K_h is small, then $h = \sqrt{K_h}$)

pH of Solution

$$\text{Consider, } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

Since, bases and acids are weaker, hence

$$[\text{BOH}] = [\text{HA}] \Rightarrow [\text{B}^+] = [\text{A}^-]$$

$$\Rightarrow K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = \frac{[\text{HA}]^2}{[\text{A}^-]}$$

$$\Rightarrow [\text{H}^+] = K_a \sqrt{K_h} = \sqrt{\frac{K_w K_a}{K_b}}$$

$$\text{pH} = -\log [\text{H}^+] = -\log \sqrt{\frac{K_w K_a}{K_b}}$$

$$\Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b)$$

$$\text{or at } 25^\circ\text{C, pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b)$$

Alternative method:

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} = K_a \times \frac{\text{Ch}}{\text{C}(1-h)} = \frac{K_a h}{(1-h)}$$

$$\text{or } \text{pH} = -\log [\text{H}^+] = -\log K_a - \log(h) + \log(1-h) = \text{p}K_a - \log(h) + \log(1-h)$$

If K_h is small, then h is also small and thus $h \approx (K_h)^{1/2}$ and $(1-h) \approx 1$. Therefore,

$$\text{pH} = \text{p}K_a - \log(h) = \text{p}K_a - \log(K_h)^{1/2} \left(\because K_h = \frac{K_w}{K_a K_b} \right)$$

$$\therefore \text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b)$$

For example: What is the pH of a 0.50 M aqueous NaCN solution? ($\text{p}K_b$ of CN^- is 4.70)

Sol. NaCN is a salt of weak acid and strong base. The pH of its aqueous solution is given by:

$$\text{pH (at } 25^\circ\text{C)} = 7 + \frac{1}{2} (\text{p}K_a + \log C)$$

Remember that of any acid and its conjugate base or vice-versa: $\text{p}K_a + \text{p}K_b = \text{p}K_w$

e.g., For acid (say HA), $\text{p}K_a$ corresponds to HA and $\text{p}K_b$ corresponds to its conjugate base: A^-

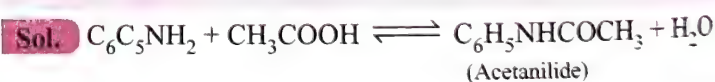
Thus, $\text{p}K_a$ of HCN = $(\text{p}K_w - \text{p}K_b) = (14 - 4.7) = 9.3$

$$\text{So, pH(at } 25^\circ\text{C)} = 7 + \frac{1}{2} (\text{p}K_a + \log C)$$

$$= 7 + \frac{1}{2} (9.3 + \log 0.5) = 11.5$$

ILLUSTRATION 8.70

Calculate the degree of hydrolysis of a mixture of aniline and acetic acid each of them being 0.01 M. K_a of acetic acid = 1.8×10^{-5} and K_b (aniline) = 4.5×10^{-10} . Also calculate pH of the mixture.



Now when we mix equal concentrations of aniline and acetic acid, they will neutralise each other to form acetanilide (salt). The salt is of weak base and weak acid, so hydrolysis takes place. The degree of hydrolysis of the salt of weak acid and weak base is given by:

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

$$\text{Here, } K_h = \frac{K_w}{K_a K_b} = \frac{10^{-14}}{1.8 \times 10^{-5} \times 4.5 \times 10^{-10}} = 1.23$$

$$\Rightarrow h = \frac{\sqrt{1.23}}{1 + \sqrt{1.23}} = \frac{1.109}{1 + 1.109} = \frac{1.109}{2.109} = 0.52$$

However the pH of solution can be calculated by using the standard result:

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b)$$

8.13 THE ACID-BASE TITRATION USING INDICATORS

The reaction between acid and base is called *neutralisation*. It is very fast and the equilibrium constant for a neutralisation reaction is so large that it nearly proceeds to completion. It is a simple and convenient volumetric method for quantitatively estimating the concentration of one if that of other is known.

A known volume of the solution of acid or base is taken in a titration flask and an indicator such as litmus solution is added to it. This solution is titrated by adding known volumes of the other solution in steps from the burette. At the end point. There is a change of colour. Litmus solution is red in the acidic region and blue in the basic region.

A number of weak organic acids (e.g., phenolphthalein, methyl orange, etc.) act as indicators if the unionised acid (HIn) and its anion (Ind^-) have different colours. the colour of the indicator is in between that of the corresponding acid (HIn) and its anion (Ind^-). Methyl orange has red colour in the acidic region and yellow colour in the basic region.

The choice of indicator depends on the abrupt change of the pH during neutralisation near the end or equivalence point.

8.13.1 pH OF MIXTURES OF ACIDS AND BASES

The rules for determining the pH of mixtures of acids and bases are as follows:

- If strong acid (S_A) or strong base (S_B) remains unused, calculate the concentration or molarity of H^+ ions and OH^- ions left in the solution and then calculate the pH or pOH accordingly.
- If weak acid (W_A) or weak base (W_B) is left behind or remains unused, a buffer (acidic or basic) is formed. Calculate the concentration of salt formed (mmoles of salt formed/volume of solution) and the concentration of W_A or W_B left behind. Use the buffer equation to calculate the pH of the solution.
- If acids or bases are completely neutralised, then salt is formed. Calculate the concentration of the salt formed and use the hydrolysis equation to calculate the pH of the solution.

Let x mmol of acid (HA) and y millimoles of base (BOH) are taken. (Note that acid is monobasic and base is monoacidic.)

8.13.2 STRONG ACID AND STRONG BASE

- If $x = y$, then complete neutralization takes place and we get $x (=y)$ millimoles of salt (BA) of strong acid and strong base which means no hydrolysis takes place and pH of solution = 7.
- If $x > y$, then there is an excess of strong acid and resulting solution is acidic with millimoles of acid left in excess = $x - y$. Now if V (in mL) be the volume of mixture, then

$$\Rightarrow M = \frac{x - y}{V}$$

Now calculate the pH using the equation $\text{pH} = -\log[\text{H}^+]$

- If $x < y$, then there is an excess of strong base and resulting solution is basic with millimoles of base left in excess = $y - x$. Now if V (in mL) be the volume of mixture, then

$$\Rightarrow M = \frac{y - x}{V}$$

Now calculate the pH using the equation $\text{pH} = 14 - \log[\text{OH}^-]$

8.13.3 STRONG BASE AND WEAK ACID

- If $x = y$, first of all complete neutralisation takes place to produce $x (=y)$ mmol of salt (BA). The salt will now undergo hydrolysis to give an alkaline solution. Calculate its pH by using standard result.

$$\text{pH} = 7 + \frac{1}{2}(\text{p}K_a + \log C)$$

C is concentration expressed in $M(\text{mol L}^{-1})$

- If $x > y$, there is excess of weak acid whose millimoles = $x - y$ and x mmol of salt is formed. This will give an acidic buffer solution. Calculate the pH of the buffer solution using the standard result:

$$\text{pH} = \text{p}K_a - \log \frac{[\text{salt}]}{[\text{acid}]} = \text{p}K_a + \log \frac{x}{x - y}$$

- If $x < y$, the solutions in this case contains excess of strong base whose millimoles are $y - x$.

$$M = \frac{y - x}{V} \text{ Calculate pH using the equation}$$

$$\text{pH} = 14 - \log [\text{OH}^-]$$

8.13.4 STRONG ACID AND WEAK BASE

- If $x = y$, first of all complete neutralisation takes place to produce $x (=y)$ mmol of salt (BA). The salt (BA) is of strong acid and weak base, hence *hydrolysis* takes place to give an acidic solution. Calculate its pH by using the standard result.

$$\text{pH} = 7 - \frac{1}{2}(\text{p}K_b + \log C) : C; \text{mol/L}$$

- If $x > y$, then solution contain excess of strong acid whose millimoles = $x - y$.

$$M = \frac{x - y}{V}$$

Now calculate pH using the equation $\text{pH} = -\log[\text{H}^+]$

- If $x < y$, then there is an excess of weak base whose millimoles are $y - x$ and millimoles of salt (BA) are x . This will give a basic buffer solution. Calculate the pH by using Henderson's equation.

$$\text{pH} = 14 - \text{p}K_a - \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= 14 - \text{p}K_b - \log \frac{x}{y - x}$$

8.13.5 WEAK ACID AND WEAK BASE

- If $x = y$, neutralisation takes place completely with the formation of $x (=y)$ mmol of salt (BA) of weak acid and weak base. So hydrolysis takes place. Calculate the pH by using:

$$\text{pH} = 7 + \frac{1}{2}(\text{p}K_a - \text{p}K_b)$$

- If $x > y$, then excess of weak acid ($x - y$) will remain with y mmol of salt. This will give an acidic buffer.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = \text{p}K_a + \log \frac{y}{x - y}$$

- If $x < y$, then excess of weak acid ($y - x$) and x mmol of salt. This will give a basic buffer.

$$\text{pH} = 14 - \text{p}K_b - \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= 14 - \text{p}K_b - \log \frac{x}{y - x}$$

13.6 ILLUSTRATION OF TITRATION OF ACIDS AND BASES

Titration of Weak Acid vs Strong Base (W_A/S_B)

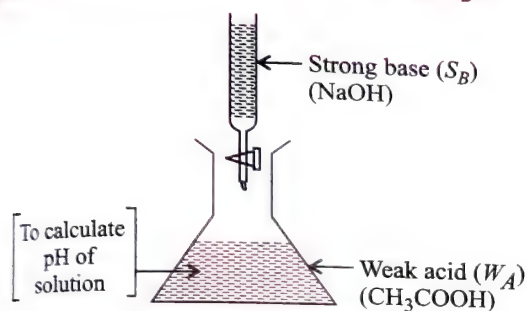


Fig. 8.2

Case I: When no titration is carried out.

It is a case of weak acid. Calculate pH by using the formula

$$\text{pH}_{W_A} = \frac{1}{2} (\text{p}K_a - \log C)$$

Case II: When the titration is < 100%.

The salt of weak acid and strong base is formed and W_A is left in the conical flask. So, acidic buffer is formed. Calculate pH by using the formula.

$$\text{pH}_{\text{acidic buffer}} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

Case III: When the titration = 100%.

Salt of W_A/S_B is formed. Calculate the pH by using hydrolysis formula.

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

Case IV: When the titration is > 100%

W_A is completely neutralised and excess of S_B is left in the conical flask. Calculate the pOH and then pH of the solution.

$$\text{pOH} = -\log [\text{OH}^-]$$

Titration of Strong Base (S_B) vs Weak Acid (W_A)

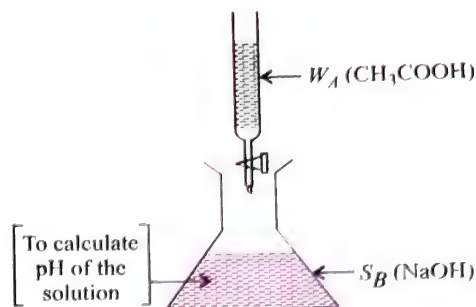


Fig. 8.3

Case I: When no titration is carried out.

It is a strong base. Calculate pOH and then pH.

$$\text{pOH} = -\log [\text{OH}^-]$$

Case II: When the titration is < 100%.

Salt of W_A and S_B is formed but strong base is left in the conical flask. So, it is a case of S_B . Calculate pOH and then pH.

$$\text{pOH} = -\log [\text{OH}^-]$$

Case III: When the titration = 100%.

Salt of W_A/S_B is formed calculate pH by using hydrolysis formula (as in type A). (Case III).

Case IV: When the titration is > 100%.

Salt of W_A and S_B is formed and excess of W_A is left in the flask. So acidic buffer is formed. Calculate the pH of the solution by using acidic buffer equation.

Titration of W_B vs S_A

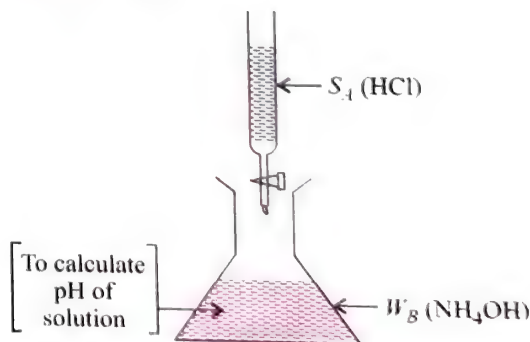


Fig. 8.4

Case I: When no titration is carried out.

It is the case of W_B . Calculate pH by using formula of W_B .

$$\text{pOH}_{W_B} = \frac{1}{2} (\text{p}K_b - \log C)$$

Case II: When the titration is < 100%.

Salt of W_B/S_A is formed and W_B is left in the flask. So basic buffer is formed. Calculate pH by using the formula.

$$\text{pOH}_{\text{Basic buffer}} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Case III: When the titration = 100%

Salt of W_B/S_A is formed. Calculate pH by using hydrolysis formula.

$$\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$$

Case IV: When the titration > 100%.

W_B is completely neutralised and excess of S_A is left in the flask. Calculate pH accordingly.

$$\text{pH} = -\log [\text{H}^{\oplus}]$$

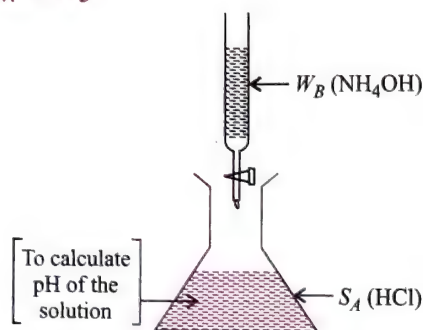
Titration S_A vs W_B 

Fig. 8.5

Case I: When no titration is carried out.

It is a case of S_A . Calculate pH accordingly.

$$\text{pH} = -\log [\text{H}^{\oplus}]$$

Case II: When the titration is < 100%.

Salt of W_B/S_A is formed but S_A is left in the flask. Calculate the pH accordingly.

$$\text{pH} = -\log [\text{H}^{\oplus}]$$

Case III: When the titration = 100%.

Salt of W_B/S_A is formed. Calculate pH by using hydrolysis formula (as in type C) (Case III).

Case IV: When the titration > 100%.

Salt of W_B/S_A is formed and excess of W_B is left in the flask. So, basic buffer is formed (as in type C, Case II).

ILLUSTRATION 8.74

Calculate the pH of the solutions when following conditions are provided:

Given: ($\text{p}K_a = 4.74$)

- 20 mL of M/10 CH_3COOH solution is titrated with M/10 solution of NaOH.
 - No titration is carried out.
 - When 16 mL of NaOH is added.
 - When 20 mL of NaOH is added.
 - When 30 mL of NaOH is added.
- 20 mL of M/10 NaOH solution is titrated with M/10 solution of CH_3COOH .
 - No titration is carried out.
 - When 18 mL of CH_3COOH is added.
 - When 20 mL of CH_3COOH is added.
 - When 40 mL of CH_3COOH is added.
- 10 mL of M/10 NH_4OH solution is titrated with M/10 solution of H_2SO_4 .

Given: ($\text{p}K_b = 4.76$).

- No titration is carried out.
 - When 4 mL of H_2SO_4 is added.
 - When 5 mL of H_2SO_4 is added.
 - When 10 mL of H_2SO_4 is added.
- 10 mL of M/10 H_2SO_4 solution is titrated with M/10 solution of NH_4OH .
 - No titration is carried out.
 - When 10 mL of NH_4OH is added.
 - When 20 mL of NH_4OH is added.
 - When 40 mL of NH_4OH is added.

Sol. a. i. When no titration is carried out (it is a case of W_A).

$$\begin{aligned} \therefore \text{pH}_{W_A} &= \frac{1}{2} (\text{p}K_a - \log C) \\ &= \frac{1}{2} \left(4.74 - \log \frac{1}{10} \right) \\ &= \frac{1}{2} (4.74 - \log 10^{-1}) = \frac{1}{2} (4.74 + 1) \\ &= 2.87 \end{aligned}$$

ii. When 16 mL of NaOH is added (acidic buffer is formed)

$$\text{mmol of } \text{CH}_3\text{COOH} = 20 \times \frac{1}{10} = 2$$

$$\text{mmol of NaOH} = 16 \times \frac{1}{10} = 1.6$$

1.6 mmol of NaOH react with 1.6 mmol of CH_3COOH , so 1.6 mmol of CH_3COONa is formed and $(2 - 1.6) = 0.4$ mmol of CH_3COOH (W_A) is left in the solution.

$$\begin{aligned} \therefore \text{pH}_{\text{acidic buffer}} &= \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= 4.74 + \log \frac{1.6/36}{0.4/36} \\ &= 4.74 + \log 4 \\ &= 4.74 + 2 \times 0.3 = 5.34 \end{aligned}$$

iii. When 20 mL of NaOH is added (salt of W_A/S_B is formed)

$$\text{mmol of } \text{CH}_3\text{COOH} = 20 \times \frac{1}{10} = 2$$

$$\text{mmol of NaOH} = 20 \times \frac{1}{10} = 2$$

$$\begin{aligned} [\text{Salt}] &= [\text{CH}_3\text{COONa}] = \frac{2 \text{ mL}}{(20 + 20) \text{ mL}} \\ &= \frac{2}{40} = 0.05 \text{ M} \end{aligned}$$

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

$$\text{pH} = \frac{1}{2} (14 + 4.74 + \log (0.05))$$

$$= \frac{1}{2} (18.74 + \log 5 \times 10^{-2})$$

$$(\log 5 \times 10^{-2}) = -2 + 0.7 = -1.3$$

$$= \frac{1}{2} (18.74 - 1.3) = 8.72$$

iv. When 30 mL of NaOH is added (it is a case of S_B)

$$\text{mmol of CH}_3\text{COOH} = 20 \times \frac{1}{10} = 2$$

$$\text{mmol of NaOH} = 30 \times \frac{1}{10} = 3$$

$$\text{mmol of NaOH left} = 3 - 2 = 1$$

$$[\text{NaOH}] = [\text{OH}^\ominus] = \frac{1}{50} = 0.02 \text{ M} = 2 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log (2 \times 10^{-2}) = 1.7$$

$$\text{pH} = 14 - 1.7 = 12.3.$$

b. i. No titration is carried out (it is a case of S_B)

$$[\text{NaOH}] = \frac{1}{10} = 10^{-1}$$

$$\text{pOH} = 1, \text{pH} = 14 - 1 = 13$$

ii. When 18 mL of CH_3COOH is added (it is a case of S_B)

$$\text{mmol of NaOH} = 20 \times \frac{1}{10} = 2$$

$$\text{mmol of CH}_3\text{COOH} = 18 \times \frac{1}{10} = 1.8$$

$$\text{mmol of NaOH left} = 2 - 1.8 = 0.2$$

$$[\text{OH}^\ominus] = \frac{0.2 \text{ mmol}}{(20 + 18) \text{ mL}} = 0.005 = 5 \times 10^{-3}$$

$$\text{pOH} = -\log (5 \times 10^{-3}) = 3 - 0.7 = 2.3$$

$$\text{pH} = 14 - 2.3 = 11.7$$

iii. When 20 mL of CH_3COOH is added (salt of W_A/S_B is formed)

Same answer as in part (a), case (iii)

$$\text{pH} = 10.02.$$

iv. When 40 mL of CH_3COOH is added (acidic buffer is formed)

$$\text{mmol of NaOH} = 2$$

$$\text{mmol of CH}_3\text{COOH} = 40 \times \frac{1}{10} = 4$$

$$\text{mmol of CH}_3\text{COOH left} = 4 - 2 = 2$$

$$\text{mmol of Salt (CH}_3\text{COONa) formed} = 2$$

$$\text{pH} = 4.74 + \log \left(\frac{2/60}{2/60} \right)$$

$$\text{pH} = 4.74$$

c. i. When no titration is carried out (it is case of W_B)

$$[\text{NH}_4\text{OH}] = \frac{1}{10} = 10^{-1} \text{ M}$$

$$\text{pOH}_{WB} = \frac{1}{2} (\text{p}K_b - \log C) = \frac{1}{2} (4.76 - \log 10^{-1})$$

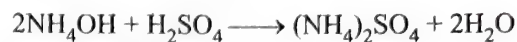
$$= \frac{1}{2} (4.76 + 1) = 2.88$$

$$\text{pH} = 14 - 2.88 = 11.12$$

ii. When 4 mL of H_2SO_4 is added (basic buffer is formed)

$$\text{mmol of NH}_4\text{OH} = 10 \times \frac{1}{10} = 1$$

$$\text{mmol of H}_2\text{SO}_4 = 4 \times \frac{1}{10} = 0.4$$



Initial	1 mmol	0.4 mmol	0	—
Final	$(1 - 2 \times 0.4)$	$(0.4 - 0.4)$	0.4 mmol	—
	= 0.2	= 0		

$$\therefore [\text{NH}_4\text{OH}]_{\text{left}} = 0.2 \text{ mmol}$$

$$\therefore [(\text{NH}_4)_2\text{SO}_4] = 0.4 \text{ mmol}$$

$$[\text{NH}_4^\oplus] = 2 \times 0.4 = 0.8 \text{ mmol}$$

$$\text{Total } V = 10 + 4 = 14 \text{ mL}$$

$$\begin{aligned} \text{pOH}_{\text{basic buffer}} &= \text{p}K_b + \log \left[\frac{0.8/14}{0.2/14} \right] \\ &= 4.76 + \log 4 \\ &= 4.76 + 2 \times 0.3 \\ &= 5.36 \end{aligned}$$

$$\text{pH} = 14 - 5.36 = 8.64$$

Alternatively: mmoles = mEq of $\text{NH}_4\text{OH} = 1$.

$$\begin{aligned} \text{mEq of H}_2\text{SO}_4 &= 4 \times \frac{1}{10} \times 2 \quad (n \text{ factor of H}_2\text{SO}_4) \\ &= 0.8 \end{aligned}$$

$$\text{mmol} = \text{mEq of } [\text{NH}_4\text{OH}]_{\text{left}} = 1 - 0.8 = 0.2$$

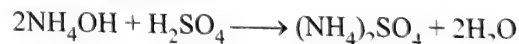
It is evident that 0.8 mEq of H_2SO_4 reacts with 0.8 mEq of NH_4OH (≈ 0.8 mmol of NH_4OH since 'n' factor is one) to give 0.8 mEq of $(\text{NH}_4)_2\text{SO}_4$.

$$\text{pOH}_{\text{basic buffer}} = \text{p}K_b + \log \left[\frac{0.8/14}{0.2/14} \right] = 5.36$$

$$\text{pH} = 14 - 5.36 = 8.64$$

iii. When 5 mL of H_2SO_4 is added (salt of W_B/S_A is formed)

According to equation:



Initial	1 mmol	$5 \times \frac{1}{10}$	0	0
		= 0.5 mmol		

Final	$(1 - 2 \times 0.5)$	$0.5 - 0.5$	0.5 mmol	
	= 0	= 0		

$$[(\text{NH}_4)_2\text{SO}_4] = 0.5 \text{ mmol},$$

$$[\text{NH}_4^\oplus] = 2 \times 0.5 = 1 \text{ mmol}$$

$$\therefore [\text{NH}_4^\oplus] = \frac{1 \text{ mmol}}{(10 + 5) \text{ mL}} = 0.06 \text{ M}$$

Alternatively:

$$\text{mEq} = \text{mmol of NH}_4\text{OH} = 1$$

$$\begin{aligned} \text{mEq of H}_2\text{SO}_4 &= 5 \times \frac{1}{10} \times 2 \quad (n \text{ factor of H}_2\text{SO}_4) \\ &= 1 \end{aligned}$$

$$[\text{Salt}] = [(\text{NH}_4)_2\text{SO}_4]$$

$$= [\text{NH}_4^+] = \frac{1 \text{ mEq}}{15 \text{ mL}} = 0.06 \text{ M}$$

$$\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$$

$$= \frac{1}{2} (14 - 4.76 - \log (6 \times 10^{-2}))$$

$$= \frac{1}{2} (14 - 4.76 + 1.22) = 5.23$$

$$\left[\begin{aligned} -(\log 6 \times 10^{-2}) &= -\log 3 - \log 2 + 2 \\ &= -0.48 - 0.3 + 2 \\ &= 1.22 \end{aligned} \right]$$

iv. When 10 mL of H_2SO_4 is added (it is a case of S_A)

$$\text{mEq} = \text{mmoles of } \text{NH}_4\text{OH} = 1$$

$$\text{mEq of } \text{H}_2\text{SO}_4 = 10 \times \frac{1}{10} \times 2 = 2$$

$$\text{mEq of } \text{H}_2\text{SO}_4 \text{ left} = 2 - 1 = 1$$

$$\text{Total } V = 10 + 10 = 20 \text{ mL}$$

$$[\text{H}^+] = \frac{1 \text{ mEq}}{20 \text{ mL}} = 0.05 = 5 \times 10^{-2}$$

$$[\text{pH}] = -\log (5 \times 10^{-2}) = 1.3$$

d. i. When no titration is carried out (it is a case of S_A)

$$[\text{H}^+] = \frac{1}{10} \times 2 \text{ (n factor of } \text{H}_2\text{SO}_4)$$

$$= 2 \times 10^{-1}$$

$$\text{pH} = -\log (2 \times 10^{-1}) = 0.7$$

ii. When 10 mL of NH_4OH is added (it is a case of S_A)

$$\text{mEq of } \text{H}_2\text{SO}_4 = 10 \times \frac{1}{10} \times 2 = 2$$

$$\text{mmol} = \text{mEq of } \text{NH}_4\text{OH} = 10 \times \frac{1}{10} = 1$$

$$\text{mEq of } \text{H}_2\text{SO}_4 \text{ left} = 2 - 1 = 1$$

$$\text{Total } V = 10 + 10 = 20 \text{ mL}$$

$$[\text{H}^+] = \frac{1 \text{ mEq}}{20 \text{ mL}} = 0.05 = 5 \times 10^{-2}$$

$$\text{pH} = -\log (5 \times 10^{-2}) = 1.3$$

iii. When 20 mL of NH_4OH is added (salt of W_B/S_A is formed)

$$\text{mEq of } \text{H}_2\text{SO}_4 = 2$$

$$\text{mEq} = \text{mmol of } \text{NH}_4\text{OH} = 20 \times \frac{1}{10} = 2$$

$$[\text{Salt}] = [(\text{NH}_4)_2\text{SO}_4] = \frac{2 \text{ mEq}}{(10 + 20) \text{ mL}} = 0.06 \text{ N}$$

$$\text{Same pH} = 5.23 \text{ (As in part C, case iii)}$$

iv. When 40 mL of NH_4OH is added (basic buffer is formed)

$$\text{mEq of } \text{H}_2\text{SO}_4 = 2$$

$$\text{mEq} = \text{mmol of } \text{NH}_4\text{OH} = 40 \times \frac{1}{10} = 4$$

$$\text{mEq of } \text{NH}_4\text{OH} \text{ left} = 4 - 2 = 2$$

2 mEq or mmol of NH_4OH reacts with 2 mEq of H_2SO_4 to give 2 mEq of $(\text{NH}_4)_2\text{SO}_4$.

$$\text{pOH}_{\text{basic buffer}} = \text{p}K_b + \log \left[\frac{2/50}{2/50} \right]$$

$$\text{pOH} = \text{p}K_b = 4.76$$

$$\text{pH} = 14 - 4.76 = 9.24$$

ILLUSTRATION 8.75

Calculate the pH of the following mixtures given ($\text{p}K_a = \text{p}K_b = 4.7447$):

- 50 mL 0.1 M NaOH + 50 mL 0.1 M CH_3COOH
- 50 mL 0.1 M NaOH + 50 mL 0.05 M CH_3COOH
- 50 mL 0.05 M NaOH + 50 mL 0.1 M CH_3COOH
- 50 mL 0.1 M NH_4OH + 50 mL 0.05 M HCl
- 50 mL 0.05 M NH_4OH + 50 mL 0.1 M HCl
- 50 mL 0.05 M NH_4OH + 50 mL 0.05 M CH_3COOH

Sol. a. 5 mEq of NaOH combines with 5 mEq of CH_3COOH and forms 5 mEq of salt of W_A/S_B .

$$[\text{salt}] = \frac{5}{100} = 0.05 \text{ M}$$

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

$$= \frac{1}{2} (14 + 4.7447 + \log 0.05) = 8.721$$

b. NaOH = $50 \times 0.1 = 5 \text{ mEq}$

$$\text{CH}_3\text{COOH} = 50 \times 0.05 = 2.5 \text{ mEq}$$

2.5 mEq of CH_3COOH reacts with 2.5 mEq of NaOH and 2.5 mEq of NaOH is left.

$$\therefore [\text{NaOH}] = [\text{OH}^-] = \frac{2.5}{100} = 2.5 \times 10^{-2}$$

$$\text{pOH} = -\log (2.5 \times 10^{-2}) = 1.6021$$

$$\text{pH} = 14 - 1.6021 = 12.3979$$

c. 2.5 mEq of NaOH combines with 5 mEq of CH_3COOH and forms 2.5 mEq of CH_3COONa .

\therefore 2.5 mEq of CH_3COOH is left. So it forms acidic buffer.

$$\text{pH} = \text{p}K_a + \log \left[\frac{\text{Salt}}{\text{Acid}} \right]$$

$$= 4.7447 + \log \left(\frac{2.5}{2.5} \right) = 4.7447$$

d. $\text{NH}_4\text{OH} = 50 \times 0.1 = 5 \text{ mEq}$

$$\text{HCl} = 50 \times 0.05 = 2.5 \text{ mEq}$$

2.5 mEq of HCl combines with 2.5 mEq of NH_4OH and forms a salt NH_4Cl (salt of S_A/W_B) and 2.5 mEq of $W_B(\text{NH}_4\text{OH})$ is left. So, it forms basic buffer.

$$\therefore \text{pOH} = \text{p}K_b + \log \left[\frac{\text{Salt}}{\text{Base}} \right]$$

$$= 4.7447 + \log \left(\frac{2.5}{2.5} \right) = 4.7447$$

$$\text{pH} = 14 - 4.7447 = 9.2553$$

$$\text{e. } \text{NH}_4\text{OH} = 50 \times 0.05 = 2.5 \text{ mEq}$$

$$\text{HCl} = 50 \times 0.1 = 5 \text{ mEq}$$

2.5 mEq of NH_4OH reacts with 2.5 mEq of HCl and forms NH_4Cl , and 2.5 mEq of HCl is left.

$$\therefore [\text{HCl}] = [\text{H}_3\text{O}^+] = \frac{2.5}{100} = 2.5 \times 10^{-2}$$

$$\text{pH} = -\log(2.5 \times 10^{-2}) = 1.6021$$

$$\text{f. } \text{NH}_4\text{OH} = 50 \times 0.05 = 2.5 \text{ mEq}$$

$$\text{CH}_3\text{COOH} = 50 \times 0.05 = 2.5 \text{ mEq}$$

2.5 mEq of NH_4OH reacts with 2.5 mEq of CH_3COOH and gives 2.5 mEq of salt ($\text{CH}_3\text{COONH}_4$) (salt of W_A/W_B), which hydrolyses.

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a - \text{p}K_b)$$

$$= \frac{1}{2}(14 + 4.7447 - 4.7447) = 7$$

ILLUSTRATION 8.76

Which of the following ions or compounds in a solution tends to produce an acidic, a basic, or a neutral solution.

- a. i. $\text{C}_2\text{H}_3\text{O}_2^-$ ii. Na^+ iii. SO_3^{2-} iv. F^-
v. NH_4^+
b. i. CH_3COONa ii. ZnCl_2 iii. KNO_3 iv. NH_4Cl
c. i. NaCN ii. K_2CO_3 iii. H_3PO_4 iv. NaF
d. i. NH_4NO_3 ii. Ba_2CO_3 iii. NaHSO_4 iv. NaOCl
v. HOCl vi. $\text{Al}(\text{NO}_3)_3$

a. (i), (iii), and (iv) are basic (since each is conjugate base of a weak acid)

(ii) Neutral (it is the conjugate acid of a strong base)

(v) Acidic (it is the conjugate base of a weak base)

b. (i) Basic (salt of W_A/S_B)

(ii) and (iv) are Acidic (salt of W_B/S_A)

(iii) neutral (salt of S_A/S_B)

c. (i), (ii), and (iv) are basic (salt of S_B/W_A)

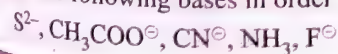
(iii) is acidic (it is a weak acid)

d. (i), (iii), (v) and (vi) are acidic (except (v), all are salt of W_B/S_A) But (v) is a weak acid.

(ii) and (iv) are basic (salt of S_B/W_A)

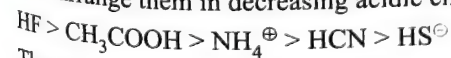
ILLUSTRATION 8.77

Arrange the following bases in order of decreasing basicity:



Sol. Stronger the acid, weaker its conjugate base and vice versa.

First arrange them in decreasing acidic character:



Therefore, the decreasing order of basic character:

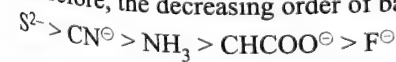


ILLUSTRATION 8.78

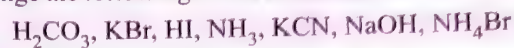
Classify each of the following as a strong acid, strong base, weak acid, and weak base:

- i. NaOH ii. HF iii. NH_4^+ iv. NH_3 v. F^- vi. HI

Sol. i. S_B ii. W_A iii. W_A iv. W_B v. S_B vi. S_A

ILLUSTRATION 8.79

Arrange the following 0.1 M solutions in order of increasing pH:



Sol. Stronger the acid, less is the pH, stronger the base, high is the pH. Increasing order of pH:

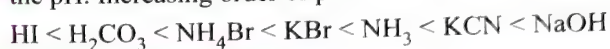


ILLUSTRATION 8.80

Why the following compounds will produce acidic solution in water?

- i. H_3PO_4 ii. CO_2 iii. HNO_2 iv. AlCl_3

Sol. a. All of them give H^+ ions in aqueous solution.

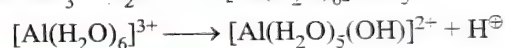
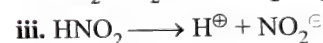
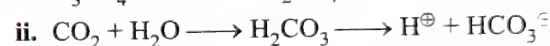
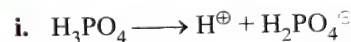


ILLUSTRATION 8.81

Write equations to explain why the following species act as weak bases in water solution.

- i. CH_3NH_2 ii. NO_2^- iii. HPO_4^{2-} iv. CHO_2^-

Sol. All of them give OH^- ions in aqueous solutions.

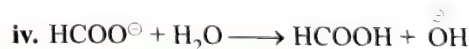
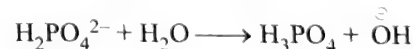
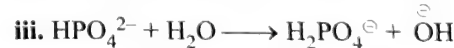
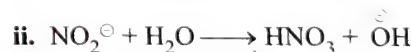
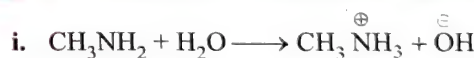


ILLUSTRATION 8.82

Which equilibrium constant(s) or ratio of equilibrium constants should be used to calculate the pH of 1.00 L of each of the following solutions?

- a. KOH b. NH_3 c. $\text{HC}_2\text{H}_3\text{O}_2$

- d. $\text{HC}_2\text{H}_3\text{O}_2 + \text{NaC}_2\text{H}_3\text{O}_2$ e. $\text{KC}_2\text{H}_3\text{O}_2$

- f. 0.10 mol $\text{HC}_2\text{H}_3\text{O}_2$ + 0.050 mol NaOH

- g. H_2S h. 0.10 NH_4Cl + 0.50 mol NaOH

- i. 0.10 mol $\text{HC}_2\text{H}_3\text{O}_2$ + 0.10 mol NaOH

- Sol.** a. $K_w(S_B)$ b. K_b and $K_w(W_B)$
 c. $K_a(W_A)$ d. K_a (Acidic buffer)
 e. $K_h = K_w/K_a$ (Salt of W_A/S_B)
 f. K_a (The solution is the same as 0.05 mol $\text{HC}_2\text{H}_3\text{O}_2$ + 0.05 mol $\text{NaC}_2\text{H}_3\text{O}_2$) (It forms acidic buffer)
 g. K_1
 h. K_b and K_w (The reaction $\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{NH}_3$ produces a basic buffer solution of NH_3 with the excess of NH_4^+)
 i. $K_h = K_w/K_a$ (The neutralised acid results in the formation of salt of W_A/S_B).

ILLUSTRATION 8.83

The salt of which one of the following five weak acid will be the most hydrolysed?

- a. HA : $K_a = 1 \times 10^{-8}$ b. HB : $K_a = 2 \times 10^{-6}$
 c. HC : $K_a = 3 \times 10^{-8}$ d. HD : $K_a = 4 \times 10^{-10}$
 e. HE : $K_a = 1 \times 10^{-7}$

Sol. d. $K_b = K_w/K_a$, so the smallest value of K_a will produce the largest value of K_b and hence the most hydrolysis.

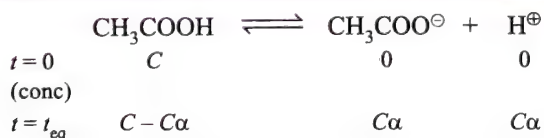
ILLUSTRATION 8.84

500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

- a. Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
 b. If 6 g of NaOH is added to the above solution, determine the final pH. [K_a of $\text{CH}_3\text{COOH} = 2 \times 10^{-5}$].

Sol. a. $[\text{CH}_3\text{COOH}]_{\text{Just after mixing}} = \frac{0.2}{2} = 0.1 \text{ M}$
 $[\text{HCl}]_{\text{Just after mixing}} = \frac{0.2}{2} = 0.1 \text{ M} = [\text{H}^+]_{\text{From HCl}}$

Note: Equal volumes are added.



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \cdot (C\alpha + 0.1)}{C - C\alpha}$$

$$[\because [\text{H}^+]_{\text{Total}} = [\text{H}^+]_{\text{From CH}_3\text{COOH}} + [\text{H}^+]_{\text{From HCl}}]$$

$$\Rightarrow C\alpha + 0.1 \approx 0.1; C - C\alpha \approx C]$$

$[\because \alpha \text{ will be small due to common ion effect}]$

$$\Rightarrow K_a \approx \alpha \times 0.1$$

$$\Rightarrow \alpha = \frac{K_a}{0.1} = 2 \times 10^{-4} \text{ [Check : } 1 - \alpha = 1 - 2 \times 10^{-4} \approx 1]$$

$$\text{and } [\text{H}^+]_{\text{Total}} = C\alpha + 0.1 = 0.1 \times 2 \times 10^{-4} + 0.1 \approx 0.1 \text{ M}$$

$$\Rightarrow \text{pH} = 1$$

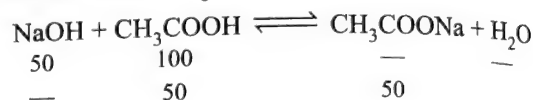
$$\text{b. } 6 \text{ g NaOH} = \frac{6}{40/1} = 0.15 \text{ mEq} \equiv 150 \text{ mmol NaOH}$$

$$\text{mmol HCl} = 500 \times 0.2 = 100 \text{ mmol}$$

NaOH will first react with HCl and if there is a leftover then it will react with CH_3COOH .

$$\Rightarrow \text{mmol NaOH left} = 150 - 100 = 50$$

These will react CH_3COOH as:



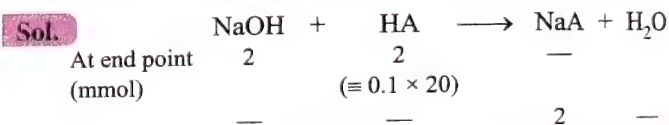
\Rightarrow Formation of an acidic buffer

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.7 + \log \frac{50/V_{\text{Total}}}{50/V_{\text{Total}}} = 4.7$$

ILLUSTRATION 8.85

0.1 M NaOH is titrated with 0.1 M, 20 mL HA till the end point. K_a (HA) = 6×10^{-6} and degree of dissociation of HA is negligible (small) as compared to unity. Calculate the pH of the resulting solution at the end point [Use $\log 6 \approx 0.8$]



Note: 20 mL of NaOH is required for the complete neutralisation of HA.

NaA is a salt of strong base and weak acid. Thus, will undergo hydrolysis and solution will become basic.

$$\text{Here } C = [\text{NaA}] = \frac{2}{20 + 20} = 0.05 \text{ M}$$

$$\text{and } \text{p}K_a = -\log(6 \times 10^{-6}) = 5.2$$

$$\text{pH}_{\text{an end point}} = 7 + \frac{1}{2} (\text{p}K_a + \log C)$$

$$= 7 + \frac{1}{2} (5.2 + \log 0.05) = 8.95$$

8.14 ILLUSTRATIONS BASED ON APPLICATIONS OF BUFFER AND SALT SOLUTION TO ELECTROCHEMISTRY

ILLUSTRATION 8.86

A hydrogen electrode placed in a solution containing sodium acetate and acetic acid in the ratio of x:y and y:x, has electrode potential values of -1.5 and -0.5 V, respectively. What is the $\text{p}K_a$ value of acetic acid?

$$E_1(\text{H}_2) = -0.059 \text{ pH}_1 = -0.059[\text{p}K_a + \log(x/y)] \quad \dots(i)$$

$$E_2(\text{H}_2) = -0.059 \text{ pH}_2 = -0.059[\text{p}K_a + \log(y/x)] \quad \dots(ii)$$

Add equations (i) and (ii), we get

$$E_1 + E_2 = -0.059 [\text{p}K_a + \log(x/y)] - 0.059 [\text{p}K_a + \log(y/x)] \\ = -2 \times 0.059 \text{ p}K_a$$

$$\text{p}K_a = \frac{-(E_1 + E_2)}{2 \times 0.059} = \frac{-(-1.5 - 0.5)}{2 \times 0.059} = \frac{0.1}{0.059} = 16.94$$

ILLUSTRATION 8.87

The emf of the following cell is observed to be 0.118 V at 25°C.



- If 30 mL of 0.2 M NaOH is added to the negative terminal of battery, find the emf of the cell.
- If 50 mL of 0.2 M NaOH is added to the negative terminal of battery, find the emf of the cell.

(a = anode, c = cathode)

$$E_{\text{H}_2} = -0.059 (\text{pH}_c - \text{pH}_a) \quad \left[\begin{array}{l} [\text{H}^+]_c = 0.1 \text{ M} \\ \text{pH} = 1 \end{array} \right]$$

$$0.118 = -0.059 (1 - \text{pH}_a)$$

$$\frac{0.118}{0.059} = 1 - \text{pH}_a$$

$$\therefore \text{pH}_a = 1 + \frac{0.118}{0.059} = 3$$

$$[\text{H}^+]_a = 10^{-3} \text{ M}$$

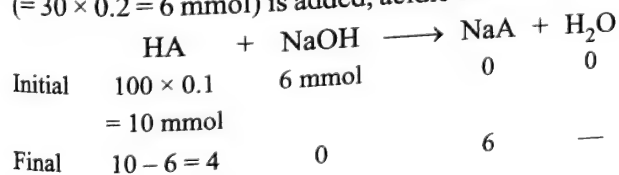
Since HA is a W_A

$$\therefore \text{pH}_{W_A} = \frac{1}{2} (\text{p}K_a - \log C)$$

$$3 = \frac{1}{2} (\text{p}K_a - \log 0.1)$$

$$\therefore \text{p}K_a = 5.$$

- When 30 mL of 0.2 M NaOH (= 30 × 0.2 = 6 mmol) is added, acidic buffer is formed.



$$\therefore [\text{Salt}] = \frac{6 \text{ mmol}}{130 \text{ mL}}$$

$$[\text{Acid}]_{\text{left}} = 10 - 6 = \frac{4 \text{ mmol}}{130 \text{ mL}}$$

$$\therefore \text{pH}_a = \text{p}K_a + \log \left(\frac{6/130}{4/130} \right)$$

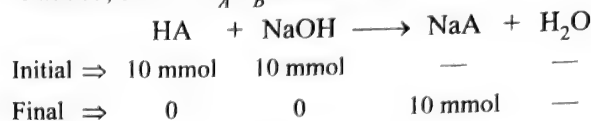
$$= 5 + \log \frac{6}{4} = 5 + \log 3 - \log 2 \\ = 5 + 0.48 - 0.3 = 5.18$$

$$E = -0.059 (\text{pH}_c - \text{pH}_a)$$

$$= -0.059 (1 - 5.18)$$

$$= 0.246 \text{ V}$$

- When 50 mL of 0.2 M NaOH (= 50 × 0.2 = 10 mmol) is added, salt of W_A/S_B is formed.



$$\therefore [\text{Salt}] = 10/150 = 0.06 \text{ M}$$

$$\therefore \text{pH}_a = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

$$= \frac{1}{2} [(14 + 5 + \log(6 \times 10^{-2}))]$$

$$= \frac{1}{2} (19 + \log 3 + \log 2 - 2)$$

$$= \frac{1}{2} (19 + 0.48 + 0.3 - 2) = 8.89$$

8.15 ILLUSTRATIONS BASED ON APPLICATIONS OF BUFFER AND SALT SOLUTION TO COLLIGATIVE PROPERTIES

ILLUSTRATION 8.88

The freezing point of 0.20 M solution of weak acid HA is 272.5 K. The molality of the solution is 0.263 mol Kg⁻¹.

- Find the pH of the solution on adding 0.25 M solution of acetate to the above solution.
- Find the pH of the solution on adding 0.20 M solution of NaOH. (K_f of water = 1.86 K m⁻¹)

Sol. a. $\Delta_f T = (273 - 272.5) = 0.5 \text{ K}, \quad \Delta_f T = iK_f m$

$$\therefore i = \Delta_f T / K_f m = 0.5 / 1.86 \times 0.263 = 1.022$$



$$\begin{array}{ccc} \text{Initial} & 1 & 0 & 0 \end{array}$$

$$\begin{array}{ccc} \text{Final} & 1 - \alpha & \alpha & \alpha \end{array}$$

$$i = 1 + \alpha \therefore 1.022 = 1 + \alpha \therefore \alpha = 0.022$$

$$K_a = C\alpha^2 = 0.2 \times (0.022)^2 = 9.6 \times 10^{-5}$$

$$\text{p}K_a = 4.0177$$

On adding 0.25 M NaA, buffer is formed.

$$\therefore [\text{Salt}] = 0.25 \text{ M}, \quad [\text{Acid}] = 0.20 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log [\text{Salt}/\text{Acid}] = 4.0177 + \log (0.25/0.20) \\ = 4.0177 + 0.0969 = 4.1146$$

- On adding 0.2 M NaOH, salt of W_A and S_B is formed

$$\therefore [\text{Salt}] = 0.2 \text{ M}$$

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

Indicator	1	2	3	4	5	6	7	8	9	10	11	12	13
Methyl orange	← Pink → 3.1–4.5				← Yellow →								
Methyl red	← Pink → 4.2–6.2			← Yellow →									
Phenolphthalein	← Colourless → 8.3–10				← Pink →								
Thymolphthalein	← Colourless → 9.3–10.5				← Pink →								
Bromothymol blue	← Orange → 6.0–7.5				← Blue →								
Bromocresol green	← Yellow → 3.8–4.6				← Blue →								

a. When a strong acid reacts with a strong base, equivalence point is the neutralisation point (i.e. pH of the solution = 7 if both acid and base have same mEq), but when a strong acid

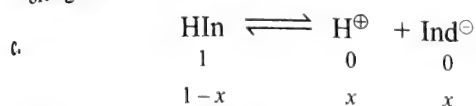
reacts with a weak base or vice-versa, pH at the equivalence point $\neq 7$ as the salt formed will get hydrolysed and pH of the solution >7 or <7 at the equivalence point. NH_4Br is a salt of strong acid and weak base.

$$\Rightarrow \text{pH} = 7 - \frac{1}{2}(\text{p}K_b + \log C)$$

$$= 7 - \frac{1}{2}(4.74 + \log 0.1) = 5.13$$

b. At $\text{pH} < 3.1$, the indicator methyl red is coloured pink; at $\text{pH} > 6.3$, it is yellow and at the intermediate values of the pH it is orange.

Since the pH of NH_4Br solution is 5.13 and it lies in the intermediate range of methyl orange, its colour will be orange. ($3.1 < \text{pH} < 6.3$)



Indicator is 80% ionised in acid form: $\Rightarrow x = 0.8$

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{Ind}^-]}{[\text{HIn}]}$$

$$\Rightarrow \text{pH} = 5.3 + \log \frac{0.8}{0.2} = 5.9$$

Table 8.6 Colours of some common indicators in different pH range

	Indicator	Colour in acidic and basic region			
		pH		pH	
a.	Methyl orange	Red	<3.1	>4.5	Yellow
b.	Bromocresol green	Yellow	<3.8	>4.6	Blue
c.	Methyl red	Pink	<4.2	>6.0	Yellow
d.	Bromocresol purple	Yellow	<5	<6.8	purple
e.	Bromothymol blue	Orange	<6.3	>7.5	blue
f.	Phenolphthalein	Colourless	<8.3	>10	pink
g.	Thymolphthalein	Colourless	<9.3	>10.5	blue

Table 8.7 Indicators and Titration

Colours of acid-base indicators

Indicator	K_a	pH value								
		3	4	5	6	7	8	9	10	11
Bromothymol blue	1×10^{-7}	Yellow	Yellow	Yellow	Yellow	Green	Blue	Blue	Blue	Blue
Methyl red	1×10^{-5}	Red	Red	Orange	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Phenolphthalein	1×10^{-9}	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Pink	Pink	Pink

$$\frac{[\text{Ind}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}^+]}$$

If $[\text{H}^+] \ll K_a$, Colour of Ind^- predominates.

If $[\text{H}^+] \gg K_a$, Colour of HIn predominates.

If $[\text{H}^+] = K_a$, equal amounts of Ind^- and HIn predominate.

Table 8.8 Some common indicators with pK values and pH ranges

Indicators	Some indicators			
	Colour		$\text{p}K_{\text{Ind}}$	pH Range
	Acid	Alkali		
Phenolphthalein	Colourless	Pink	9.3	8.0–9.8
Methyl orange	Red	Yellow	3.7	3.1–4.5
Methyl red	Red	Yellow	5.1	4.2–6.3
Phenol red	Yellow	Red	7.9	6.8–8.4
Bromothymol blue	Yellow	Blue	7.0	6.0–7.6
Thymol blue	Yellow	Purple	8.9	8.6–9.6
Litmus	Red	Blue	6.5	4.6–8.3

8.16.1 SELECTION OF INDICATORS (S_A AND S_B)

In the titration involving a strong acid and a strong base, the pH of a solution changes from about 3.3 to 10.5 near the end point with a

value of 7 at the end point. Thus, any indicator whose pH range lies between 3.3 and 10.5 would be suitable, but the most ideal would be that which shows colour changes very near to the end point ($\text{pH} = 7$). Thus, bromothymol blue having pH range between 6.0 and 7.6 is the most suitable. *Phenolphthalein* (pH range 8.0–9.8) and *methyl orange* (pH range 3.1–4.5) are the most commonly used indicators. *Phenolphthalein* is, however, the most suitable indicator when alkali is used as titrant, while *methyl orange* is most suitable when acid is used as titrant.

8.16.2 ACID-BASE TITRATION CURVES

Titration curve: It is a curve in which the pH of the solution is titrated against the volume of the titrate added.

a. Strong acid and strong base: (HCl vs NaOH)

In this case, both the titrants are completely ionised.



As OH^- is added to an acid solution, $[\text{H}^+]$ decreases and $[\text{OH}^-]$ increases \Rightarrow pH goes on increasing. As the equivalence point is reached, $[\text{H}^+]$ is rapidly reduced. Above this point $[\text{OH}^-]$ increases rapidly from 10^{-7} M and after that pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

The difference in the volume of NaOH solution between the end point and the equivalence point is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point and most of them change their colour across this pH change.

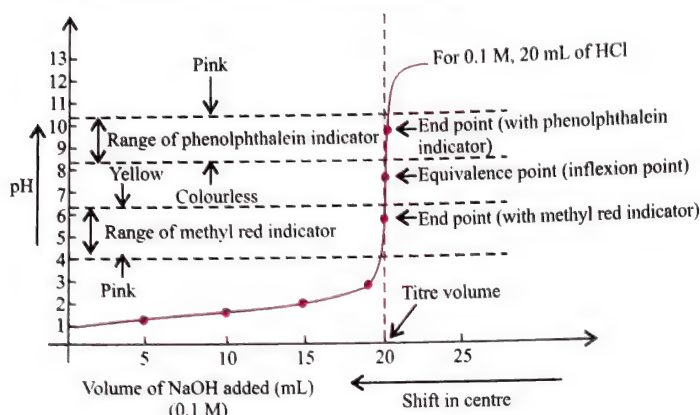


Fig. 8.7 Titration of S_A with S_B (HCl with NaOH)

b. Weak acid (W_A) and strong base (S_B) (CH_3COOH vs NaOH)

When a weak acid (say CH_3COOH) is titrated against a strong base (e.g. NaOH), the pH range near the end point is 8 to 10. Since the pH near the end point lies on the alkaline side, phenolphthalein (pH range 8.0–9.8) and thymol blue (pH range 8.6–9.6) are suitable indicators for such titrations. Methyl orange (pH range 3.1–4.5) cannot be used for such titrations.

Initially, when a few drops of OH^- are added to the weak acid, it forms an acidic buffer $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ and thus, pH of the solution changes slowly. At the equivalence point, solution will be alkaline. If OH^- addition is continued after the equivalence point $[\text{OH}^-]$ will increase rapidly.

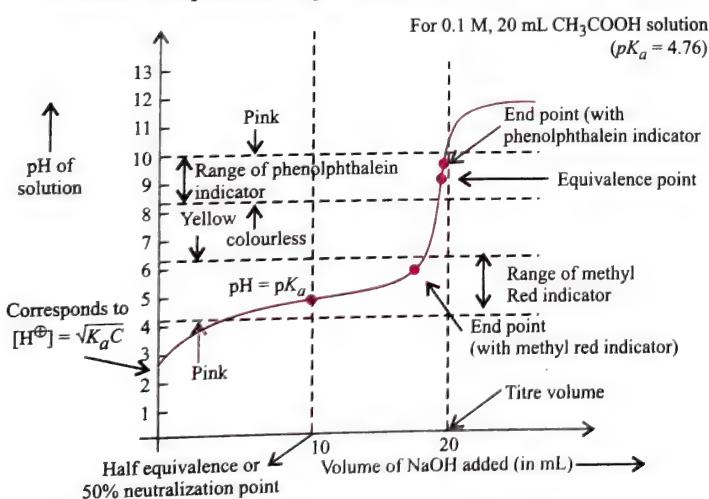


Fig. 8.8 Titration of W_A vs S_B (CH_3COOH with NaOH)

$$\begin{aligned} (\text{pH}) \text{ at equivalence point} &= 7 + \frac{1}{2} (4.76 + \log C) \\ &= 7 + \frac{1}{2} (4.76 + \log 0.05) = 8.72 \end{aligned}$$

(Here C = concentration of the salt formed at equivalence point)

Also, note that the buffer capacity of the buffer solution will be maximum at 50% equivalence point, i.e. when the volume of NaOH 10 mL.

c. Strong acid (S_A) and weak base (W_B) (HCl vs NH_4OH)

In the titration of a weak base (say NH_4OH) against a strong acid (say HCl), the pH range near the point lies in the acid range 3.0–6.0. The pH at the end point lies between 3 and 6. For such titrations, methyl orange (pH range 3.1–4.5), methyl red (pH range 4.2–6.3) and bromophenol blue (3.1–4.6) are thus the suitable indicators. Phenolphthalein can not be used for such titrations because its pH range is 9.0–9.8.

Initially, when a few drops of H^+ are added to the weak acid, it forms a basic buffer $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ and thus, pH of the solution changes slowly. At the equivalence point, solution will be acidic. If H^+ addition is continued after the equivalence point, $[\text{H}^+]$ will increase rapidly.

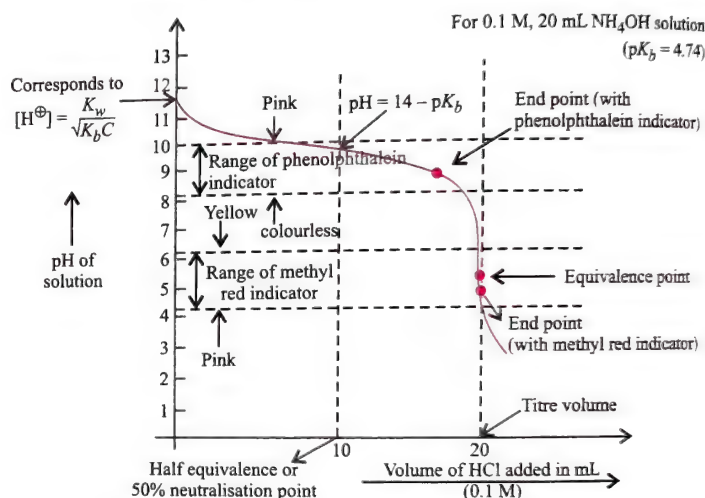


Fig. 8.9 Titration of W_B with S_A (NH_4OH with HCl)

Also note that the buffer capacity of the buffer solution will be maximum at 50% equivalence point, i.e. when the volume of HCl is 10 mL.

Note: The selection of an indicator therefore is determined by the pH of the solution at the equivalence point.

d. Weak acid (W_A) and weak base (W_B) (CH_3COOH vs NH_4OH)

When a weak acid (say CH_3COOH) is titrated against a weak base (say NH_4OH), there is no sharp change in the pH value near the end point. The pH changes during such titrations are very small and the pH varies very slowly between 6.0 and 8.0 and so no indicator can function satisfactorily in such titrations. Approximate end point is possible during phenol red (pH range 6.8–8.4).

In general, the selection of indicators for acid-base titration depends on the change in the pH at the equivalence point. The change in the pH at the equivalence point for different titrations can be calculated in the following manner.

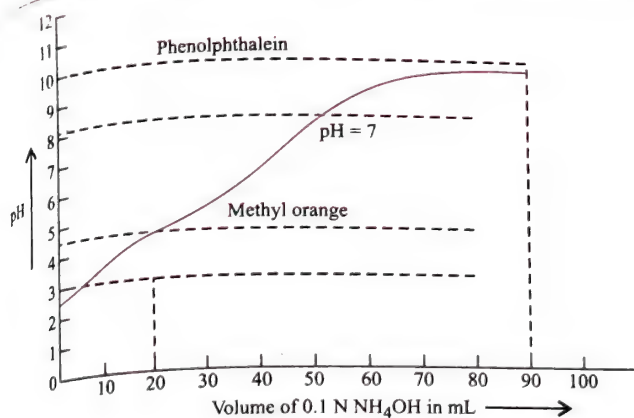


Fig. 8.10 Titration of W_A and W_B (CH_3COOH with NH_4OH)

8.16.3 DETERMINATION OF APPROXIMATE pH OF AN INDICATOR

The approximate pH of a solution can be determined by comparing its effects on different indicators or on papers impregnated with their solutions.

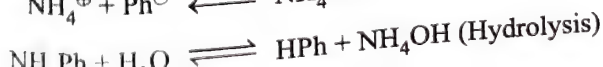
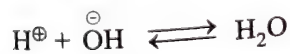
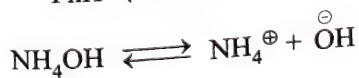
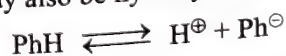
Suppose that the following colours were obtained when drops of an unknown solution were mixed with drops of indicator solution on a spot plate:

Indicator	Colour
Thymol blue	Yellow
Methyl orange	Orange or yellow
Methyl red	Yellow
Phenol red	Yellow
Phenolphthalein	Colourless

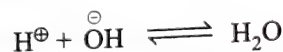
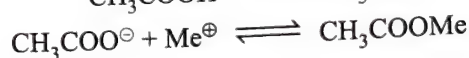
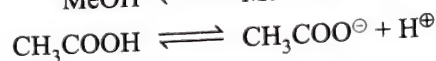
The yellow colour with thymol blue indicates that the pH of the solution lies in the range $\text{pH} = 2.8 - 8.0$. Because no red colour is produced with phenolphthalein, the pH does not exceed 8.0. The orange colour of methyl orange indicates that $\text{pH} > 4.4$ and the yellow colour of methyl red indicates that $\text{pH} > 6.2$. Since phenol red was turned yellow, the pH must be yellow. Therefore, pH must be in the range 6.2–6.8 or roughly 6.5.

It is, however, not necessary to use all the indicators. It is convenient to use the so-called *universal indicators*, which are indicator mixtures changing colour over a wide range of pH.

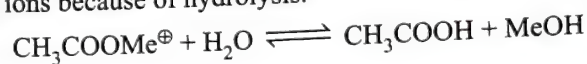
Why phenolphthalein is not suitable for the titration of strong acid with a weak base (HCl vs NH_4OH)? This is due to the fact that the weak base NH_4OH furnishes a small amount of OH^- ions which combine with H^+ ions furnished by the indicator. These OH^- ions are not sufficient to shift the equilibrium towards the right and so pink colour does not appear just at the end point. In order to get pink colour, an excess of NH_4OH has to be added. Moreover, NH_4Ph may also be hydrolysed by water.



Why methyl orange is not suitable for titration of strong base against a weak acid (CH_3COOH) vs NaOH ? Here, CH_3COOH being a weak acid does not furnish sufficient number of H^+ ions. These H^+ ions are not sufficient to combine with sufficient number of OH^- ions of methyl orange to form water and to shift the equilibrium in favour of red-coloured Me^+ ions.



Moreover, the salt CH_3COOMe does not furnish sufficient red ions because of hydrolysis.



8.16.4 END POINT AND EQUIVALENCE POINT OF A TITRATION

It should be noted that the endpoint is a point at which the titration is stopped, while equivalence point is the point at which the acid and base for oxidising and reducing agent) have been added in equivalent quantities.

- $\text{p}K_{\text{Ind}}$ of phenolphthalein is 9.3. Hence, it is an effective indicator or in the pH range 8.3–10.3.
- Phenolphthalein is not suitable for the titration of strong acid with a weak base (HCl vs NH_4OH) and methyl orange is not suitable for titration of a strong base against a weak acid (e.g. CH_3COOH vs NaOH).
- If $\text{pH} \leq \text{p}K_{\text{Ind}} - 1$, we see the colour of the acid form. If $\text{pH} = \text{p}K_{\text{Ind}}$ we see the colour of the mixture of equal amounts of acidic and basic forms. If $\text{pH} \geq \text{p}K_{\text{Ind}} + 1$, we see the colour of the basic form. Any aqueous solution to which indicator is added will necessarily contain both H_{Ind} and Ind^- .
- If $[\text{HIn}]/[\text{Ind}^-] > 10$, we see the colour of acid form. If $[\text{HIn}]/[\text{Ind}^-] < 1/10$, we see the colour of the basic form. If $[\text{HIn}]/[\text{Ind}^-]$ is less than 10 but greater than 1/10, we see the colour of both the forms in equal amounts.

Table 8.9 Indicators used in different titrations

Type of titration	Indicators used
a. S_A vs S_B	Any of the following: phenolphthalein or methyl red or methyl orange or bromothymol or thymolphthalein. (Note: Phenolphthalein is suitable when S_B is titrant. Methyl orange is suitable when S_A is titrant.)
b. W_A vs S_B	Phenolphthalein or thymolphthalein
c. S_A vs W_B	Methyl red or methyl orange or bromocresol green
d. W_A vs W_B	No suitable indicator. However, phenol red is suitable

e. Universal indicator: It is a mixture of number of indicators which shows colour changes over different pH ranges.

Colour:	Red	Orange	Yellow	Green	Blue	Purple
pH:	2	4	6	8	10	12

8.16.5 PROOF FOR THE COLOUR CHANGE, WHEN $pK_{\text{Ind}} = \text{pH}$ AT THE EQUIVALENT POINT

Acid-base indicators are weak organic acids or weak organic bases. Let the weak organic acid indicator is represented by HIn. It dissociates in aqueous solution as:



HIn and In^{\ominus} have different colours. The equilibrium constant K_{Ind} is:

$$K_{\text{Ind}} = [\text{H}^{\oplus}] [\text{In}^{\ominus}] / [\text{HIn}] \quad \dots(\text{i})$$

The exact point of the colour change will be at pH when

$[\text{HIn}] = [\text{In}^{\ominus}]$, thus, from equation (i),

$$K_{\text{Ind}} = [\text{H}^{\oplus}] \text{ or } -\log K_{\text{Ind}} = -\log[\text{H}^{\oplus}]$$

$$\text{i.e. } pK_{\text{Ind}} = \text{pH}$$

Hence, the indicator selected should be such for which $pK_{\text{Ind}} = \text{pH}$ of the solution at equivalence point.

For example, in the titration of HF with NaOH, pH at the equivalence point is 8.1. pK_{Ind} for cresol red is 8.1.

Hence, cresol red indicator is used in this titration.

8.16.6 EXPLANATION OF THE pH RANGE OF 2 UNITS OF INDICATORS

It is evident from Table 8.7 that most of the indicators have a useful colour change over a pH range of 2 units.

For example, phenolphthalein changes from colourless to pink in the pH range (8.0–9.8). Therefore, sometimes it is not possible to have an indicator for which pK_{Ind} is exactly equal to the pH at equivalence point. Consider indicator HIn.



$$K_{\text{Ind}} = [\text{H}^{\oplus}] [\text{In}^{\ominus}] / [\text{HIn}] \quad \dots(\text{i})$$

The human eye is sensitive to colour differences only when the ratio $[\text{In}^{\ominus}] / [\text{HIn}]$ is greater than 10 or smaller than 0.1.

Thus to see the acidic colour

$$\frac{[\text{In}^{\ominus}]}{[\text{HIn}]} = \frac{1}{10}$$

and to see the basic colour

$$\frac{[\text{In}^{\ominus}]}{[\text{HIn}]} = \frac{10}{1}$$

Note:

$$\frac{[\text{In}^{\ominus}]}{[\text{HIn}]} = \frac{k_a}{[\text{H}^{\oplus}]}$$

(i) If $\text{H}^{\oplus} \ll k_a$, of In^{\ominus}

- (ii) If $\text{H}^{\oplus} \gg k_a$, of $[\text{HIn}]$ predominates
(iii) If $\text{H}^{\oplus} = k_a$, colour of both predominates

Rearranging equation (i),

$$[\text{H}^{\oplus}] = K_{\text{Ind}} \frac{[\text{HIn}]}{[\text{In}^{\ominus}]}$$

\therefore For acidic colour to be visible,

$$[\text{H}^{\oplus}] = 10 K_{\text{Ind}}$$

$$\text{or } -\log [\text{H}^{\oplus}] = -\log 10 - \log K_{\text{Ind}}$$

$$\text{i.e., } \text{pH} = pK_{\text{Ind}} - 1$$

For basic colour to be visible,

$$[\text{H}^{\oplus}] = \frac{1}{10} K_{\text{Ind}}$$

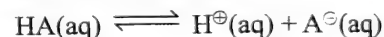
$$\text{or } -\log [\text{H}^{\oplus}] = \log 10 - \log K_{\text{Ind}}$$

$$\text{i.e., } \text{pH} = pK_{\text{Ind}} + 1$$

\therefore i.e., pH range for colour change is from $pK_{\text{Ind}} - 1$ to $pK_{\text{Ind}} + 1$, i.e. pH range of 2 units.

8.16.7 CALCULATION OF pK_a OR pK_b VALUES FROM pH OF EQUIVALENCE POINT

The pK_a of weak acid or pK_b of weak base can be determined from the measurement of pH at the equivalence point from the titration curve. For example, for a weak acid, HA.



$$K_a = [\text{H}^{\oplus}] [\text{A}^{\ominus}] / [\text{HA}]$$

$$[\text{H}^{\oplus}] = \frac{[\text{HA}]}{[\text{A}^{\ominus}]} \cdot K_a$$

$$\text{or } -\log [\text{H}^{\oplus}] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^{\ominus}]}$$

$$\text{i.e., } \text{pH} = pK_a - \log \frac{[\text{HA}]}{[\text{A}^{\ominus}]}$$

The half equivalence point is the point in the neutralisation at which one half of HA is neutralised in the reaction.



At this point, $[\text{HA}] = [\text{A}^{\ominus}]$

$$\therefore \text{pH} = pK_a - \log 1 = pK_a$$

Thus at the half equivalence point $\text{pH} = pK_a$.

Similarly, for the neutralisation of weak base, at the half equivalence point $\text{pOH} = pK_b$.

ILLUSTRATION 8.90

Methyl red has a $K_a = 10^{-5}$. The acid form HIn is red and its conjugate base, Ind^{\ominus} is yellow. Complete the following table:

pH	3	5	7
$[\text{Ind}^{\ominus}] / [\text{HIn}]$	—	—	—
Colour	—	—	—

Sol. 10^{-2} , 1, 10^2 , Red, Orange, Yellow.

i. $\text{pH} = 3$, $[\text{H}^{\oplus}] = 10^{-3} \text{ M}$

$$\left[\frac{\text{Ind}^{\ominus}}{\text{HIn}} \right] = \frac{K_a}{[\text{H}^{\oplus}]} = \frac{10^{-5}}{10^{-3}} = 10^{-2}$$

(Colour of acid form predominates, i.e. red)

ii. $\text{pH} = 5, [\text{H}^{\oplus}] = 10^{-5} \text{ M}$

$$\therefore \left[\frac{\text{Ind}^{\ominus}}{\text{HIn}} \right] = \frac{10^{-5}}{10^{-5}} = 1$$

(Colour is mixture of red and yellow, i.e. orange)

iii. $\text{pH} = 7, [\text{H}^{\oplus}] = 10^{-7} \text{ M}$

$$\left[\frac{\text{Ind}^{\ominus}}{\text{HIn}} \right] = \frac{10^{-5}}{10^{-7}} = 10^2$$

(Colour of basic form predominates, i.e., yellow colour)

ILLUSTRATION 8.91

There are three acid-base indicators: methyl orange (end point at $\text{pH} = 4$), bromothymol blue (end point $\text{pH} = 7$), and phenolphthalein (end point at $\text{pH} = 9$). Which of the following would you select for the titrations?

- a. H_2SO_4 with KOH b. KCN with HCl
c. NH_3 with HNO_3 d. HF with NaOH

- a. Any (S_A vs S_B)
b. Methyl orange (S_A vs salt of W_A/W_B)
c. Methyl orange (S_A vs W_B)
d. Phenolphthalein (W_A vs S_B)

ILLUSTRATION 8.92

A solution gives the following colours with different indicators:

- a. Methyl orange \Rightarrow Yellow
b. Methyl red \Rightarrow Yellow
c. Bromothymol blue \Rightarrow Orange

What is the pH of the solution?

- a. The colour in methyl orange indicates that $\text{pH} > 4.5$. [Methyl orange is Red in acidic ($\text{pH} < 3.1$) and yellow in basic ($\text{pH} > 4.5$)]
b. The colour in methyl red indicates that $\text{pH} > 6.0$. [Methyl red is Pink in acidic ($\text{pH} < 4.2$) and yellow in basic ($\text{pH} > 6.0$)]
c. The colour in bromthymol blue indicates that $\text{pH} < 6.3$ [bromthymol blue is orange in acidic ($\text{pH} < 6.3$) and blue in basic ($\text{pH} > 7.5$)]
Therefore, the pH of the solution is between 6.0 to 6.3.

ILLUSTRATION 8.93

What indicators will be suitable for the following acid-base titrations?

- a. HCOOH against NaOH
b. HBr against KOH
c. NH_4OH with HNO_3

Sol.

- a. Phenolphthalein and thymolphthalein are suitable for the titration of W_A and S_B .
b. Bromothymol blue, phenolphthalein, methyl orange, and thymolphthalein are suitable for the titration of S_A and S_B .
c. Methylorange, bromocresol green, and methyl red are suitable for the titration of W_B and S_A .
(Refer Table 8.6 and Fig. 8.7 to 8.9)

ILLUSTRATION 8.94

Calculate the pH at which an acid indicator with $K_a = 1.0 \times 10^{-5}$ changes colour when the indicator is $1.00 \times 10^{-3} \text{ M}$.

Sol. The midpoint of the colour change range of an indicator is the point at which its acid and conjugate base forms are present in equal concentration, hence

$$K_{\text{ind}} = \frac{[\text{H}_3\text{O}^{\oplus}][\text{Ind}^{\ominus}]}{[\text{HIn}]} = [\text{H}_3\text{O}^{\oplus}] = 1.0 \times 10^{-5}$$

and $\text{pH} = 5.00$

ILLUSTRATION 8.95

At what pH will a $1.0 \times 10^{-3} \text{ M}$ solution of an indicator with $K_b = 1.0 \times 10^{-10}$ change colour?

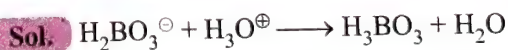
Sol. The indicator changes colour when the conjugates are equal to concentration.

$$K_b = \frac{[\text{HIn}][\text{OH}^{\ominus}]}{[\text{Ind}^{\ominus}]} = [\text{OH}^{\ominus}] = 1.0 \times 10^{-10}$$

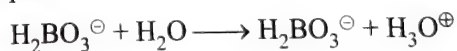
thus $\text{pOH} = 10.00$ and $\text{pH} = 4.00$

ILLUSTRATION 8.96

What indicator should be used for the titration of $0.10 \text{ M KH}_2\text{BO}_3$ with 1.10 M HCl ?



At equivalence point, $0.050 \text{ M H}_3\text{BO}_3$ would be produced. Only the first ionisation step of H_3BO_3 is important to the pH.



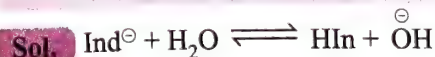
$$K_a = \frac{[\text{H}_3\text{O}^{\oplus}][\text{H}_2\text{BO}_3^{\ominus}]}{[\text{H}_3\text{BO}_3]} = \frac{x^2}{0.050} = 7.3 \times 10^{-10}$$

Thus $x = 6.0 \times 10^{-6}$ and $\text{pH} = 5.22$

pH 5.22 is in the middle of the range of methyl red which would therefore be suitable.

ILLUSTRATION 8.97

Calculate the pH at which an indicator with $\text{p}K_b = 4$ changes colour.



At the colour change, $[\text{Ind}^{\ominus}] = [\text{HIn}]$

$$K_b = \frac{[\text{OH}^{\ominus}][\text{HIn}]}{[\text{Ind}^{\ominus}]} = 1.0 \times 10^{-4} = [\text{OH}^{\ominus}]$$

and $\text{pOH} = 4.0$

$$\therefore \text{pH} = 10.00$$

ILLUSTRATION 8.98

Bromophenol blue is an indicator with a K_a value of 5.84×10^{-5} . What is the percentage of this indicator in its basic form at a pH of 4.84?

Sol. $K_a = 5.84 \times 10^{-5}$; $\text{p}K_a = 4.2336$

$$\text{pH} = \text{p}K_a + \log [\text{Ind}^{\ominus}/\text{HIn}]$$

$$4.84 = 4.2336 + \log [\text{Ind}^{\ominus}/\text{HIn}]$$

$$\therefore \log [\text{Ind}^{\ominus}/\text{HIn}] = 0.6064,$$

$$[\text{Ind}^{\ominus}/\text{HIn}] = 4.04$$

$$\% \text{ of basic form} = \frac{[\text{Ind}^{\ominus}]}{[\text{Ind}^{\ominus}] + [\text{HIn}]} \times 100$$

$$[\text{HIn}/\text{Ind}^{\ominus}] = 1/4.04$$

Add 1 to both sides of equation (i)

$$\frac{[\text{HIn}]}{[\text{Ind}^{\ominus}]} + 1 = \frac{1}{4.04} + 1 \quad \therefore \frac{[\text{HIn}] + [\text{Ind}^{\ominus}]}{[\text{Ind}^{\ominus}]} = \frac{5.04}{4.04}$$

$$\frac{[\text{Ind}^{\ominus}]}{[\text{HIn}] + [\text{Ind}^{\ominus}]} \times 100 = \frac{4.04}{5.04} \times 100 = 80\%$$

ILLUSTRATION 8.99

An acid-base indicator has a K_a of 3.0×10^{-5} . The acid form of the indicator is red and the basic form is blue. (a) By how much must the pH change in order to change the indicator from 75% red to 75% blue?

Sol.	$\text{HIn} \rightleftharpoons \text{H}^{\oplus} + \text{Ind}^{\ominus}$
	Acid form Conjugate base or salt
i.	75% red 25% blue
ii.	25% red 75% blue

When indicator is 75% red \Rightarrow 25% blue (basic form)

$$\text{a. } \therefore \text{pH}_1 = \text{p}K_a + \log(25/75) = \text{p}K_a + \log 1/3 \quad \dots(i)$$

When acid form of indicator is 75% blue \Rightarrow 25% red,

$$\text{pH}_2 = \text{p}K_a + \log(75/25) = \text{p}K_a + \log 3 \quad \dots(ii)$$

From equations (i) and (ii)

$$\begin{aligned} \text{pH}_2 - \text{pH}_1 &= \log 3 - \log 1/3 = \log 9 = \log (3)^2 \\ &= 0.4771 \times 2 = 0.9542 \end{aligned}$$

$$\therefore \text{Change in pH} = 0.9452$$

ILLUSTRATION 8.100

- At what pH does indicator change colour if the indicator is a weak acid with $K_{\text{Ind}} = 4.0 \times 10^{-4}$?
- For which of the following neutralisation would the indicator be useful?

i. $\text{HCl} + \text{NaOH}$

ii. $\text{CH}_3\text{COOH} + \text{NaOH}$

iii. $\text{HCl} + \text{NH}_3$

c. Name the indicators which can be used for such titration.

Sol.

- The mid-point of the colour change range of an indicator is the point at which its acid and conjugate base forms are present in equal concentration.

$$\begin{aligned} \text{pH} &= \text{p}K_{\text{Ind}} = -(\log K_{\text{Ind}}) \\ &= -\log (4 \times 10^{-4}) \\ &= -\log 2^2 + 4 \\ &= -0.6 + 4 = 3.4 \end{aligned}$$

- pH range of the indicator is 3.4 and is suitable for the titration of S_A/W_B ($\text{HCl} + \text{NH}_3$).
- The pH at the end point lies between 3.0 and 6.0. For such titrations, methyl orange (pH range 3.1–4.5), methyl red (pH range 4.2–6.3), and bromophenol blue (3.1–4.6) are thus the suitable indicators.

ILLUSTRATION 8.101

The acid form of an acid base indicator is yellow in acid and red in basic form. What is the change in pH in order to change the indicator from 80% yellow to 80% red.

Sol.

	$\text{HIn} \rightleftharpoons \text{H}^{\oplus} + \text{Ind}^{\ominus}$
	Acid form Base form
First case:	80% yellow 20% red
Second case:	20% yellow 80% red

First case:

$$\begin{aligned} \text{pH}_1 &= \text{p}K_a + \log \frac{[\text{Ind}^{\ominus}]}{[\text{HIn}]} \\ &= \text{p}K_a + \log \left(\frac{20}{80} \right) \\ &= \text{p}K_a + \log 1/4 \quad \dots(i) \end{aligned}$$

Second case:

$$\begin{aligned} \text{pH}_2 &= \text{p}K_a + \log \left(\frac{80}{20} \right) \\ &= \text{p}K_a + \log 4 \quad \dots(ii) \end{aligned}$$

From equations (i) and (ii), we get

$$\text{pH}_2 - \text{pH}_1 = 2 \log 4 = 4 \log 2 = 4 \times 0.3 = 1.2$$

CONCEPT APPLICATION EXERCISE 8.3

Objective questions

Buffer solution

- Which of the following is a buffer solution?
 - A solution of KCl and KOH
 - A solution of $\text{CH}_3\text{COONH}_4$
 - A solution of K_2SO_4 and NH_4OH
 - A solution of PhCOOK and PhCOOH

2. Which of the following is not a buffer?

- (1) $\text{NH}_4\text{OH} + \text{C}_6\text{H}_5\text{COOH}$
- (2) $\text{HCOOH} + \text{HCOONa}$
- (3) $\text{H}_2\text{CO}_3 + \text{HCOOK}$
- (4) $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4$

3. In an acidic buffer solution, if some H_2SO_4 is added, its pH will

- (1) Remain constant
- (2) Change but cannot be predicted
- (3) Decrease
- (4) Increase

4. Which of the following solutions containing weak acid and salt of its conjugate base has maximum buffer capacity?

- (1) $[\text{Salt}] < [\text{Acid}]$
- (2) $[\text{Salt}] = [\text{Acid}]$
- (3) $[\text{Salt}] > [\text{Acid}]$
- (4) $[\text{Salt}] + [\text{Acid}]$ is minimum

5. A weak acid HA has $K_a = 10^{-6}$. What would be the molar ratio of this acid and its salt with strong base so that pH of the buffer solution is 5?

- (1) 1/10
- (2) 10
- (3) 1
- (4) 2

6. The addition of NaH_2PO_4 to 0.1 M H_3PO_4 will cause

- (1) No change in pH value
- (2) Increase in its pH value
- (3) Decrease in its pH value
- (4) Change in pH but cannot be predicted

7. On diluting a buffer solution, its pH

- (1) Increases
- (2) Decreases
- (3) Remains same
- (4) Cannot be predicted

8. The pH of a solution containing 0.1 mol of CH_3COOH , 0.2 mol of CH_3COONa , and 0.05 mol of NaOH in 1 L. (pK_a of $\text{CH}_3\text{COOH} = 4.74$) is:

- (1) 5.44
- (2) 5.20
- (3) 5.04
- (4) 4.74

9. A weak base BOH is titrated with strong acid HA. When 10 mL of HA is added, the pH is 9.0 and when 25 mL is added, pH is 8.0. The volume of acid required to reach the equivalence point is

- (1) 50 mL
- (2) 40 mL
- (3) 35 mL
- (4) 30 mL

10. To 1.0 L solution containing 0.1 mol each of NH_3 and NH_4Cl , 0.05 mol NaOH is added. The change in pH will be (pK_a for $\text{CH}_3\text{COOH} = 4.74$)

- (1) 0.30
- (2) -0.30
- (3) 0.48
- (4) -0.48

11. The pH of blood is 7.4. If the buffer in blood constitute CO_2 and HCO_3^- ions, calculate the ratio of conjugate base to acid (H_2CO_3) to maintain the pH of blood. Given K_1 of $\text{H}_2\text{CO}_3 = 4.5 \times 10^{-7}$.

- (1) 11.25
- (2) 10.0
- (3) 8.5
- (4) None

12. The pH of blood is

- (1) >10
- (2) Between 8 and 0
- (3) Between 7 and 8
- (4) <6

13. Buffer in blood consists of

- (1) H_2CO_3 and Cl^-
- (2) HCl and HCO_3^-
- (3) HCl and Cl^-
- (4) H_2CO_3 and HCO_3^-

14. K_a for HCN is 5×10^{-10} at 25°C . For maintaining a constant pH of 9.0, the volume of 5 M KCN solution required to be added to 10 mL of 2 M HCN solution is

- (1) 9.3 mL
- (2) 7.95 mL
- (3) 4 mL
- (4) 2 mL

15. 18 mL of mixture of CH_3COOH and CH_3COONa required 6 mL of 0.1 M NaOH for neutralisation of the acid 12 mL of 0.1 M HCl for reaction with salt, separately. If pK_a of the acid is 4.75, what is the pH of the mixture

- (1) 4.5
- (2) 4.6
- (3) 4.75
- (4) 5.05

16. The pH of blood is maintained by the balance between H_2CO_3 and NaHCO_3 . If the amount of CO_2 in the blood is increased, how will it effect the pH of blood?

- (1) pH will remain same.
- (2) pH will be 7.
- (3) pH will increase.
- (4) pH will decrease.

17. Fixed volume of 0.1 M benzoic acid ($pK_a = 4.2$) solution is added into 0.2 M sodium benzoate solution and formed a 300 mL, resulting acidic buffer solution. If pH of the resulting solution is 3.9, then added volume of benzoic acid is

- (1) 240 mL
- (2) 150 mL
- (3) 100 mL
- (4) None

18. 0.1 mol of RNH_2 ($K_b = 5 \times 10^{-5}$) is mixed with 0.08 mol of HCl and diluted to 1 L. Calculate the $[\text{H}^+]$ in the solution.

- (1) 8×10^{-11} M
- (2) 1.6×10^{-11} M
- (3) 8×10^{-5} M
- (4) 8×10^{-2} M

Hydrolysis of salt

19. A weak acid HX ($K_a = 10^{-5}$) on reaction with NaOH gives NaX . For 0.1 M aqueous solution of NaX , the % hydrolysis is

- (1) 1%
- (2) 0.01%
- (3) 0.001%
- (4) 0.15%

20. The pH of 0.1 M solution of the following salts decreases in the order

- (1) $\text{HCl} > \text{NaCl} > \text{NH}_4\text{Cl} > \text{NaCN}$
- (2) $\text{HCl} > \text{NaCN} > \text{NH}_4\text{Cl} > \text{NaCl}$
- (3) $\text{NaCN} > \text{NaCl} > \text{NH}_4\text{Cl} > \text{HCl}$
- (4) $\text{NH}_4\text{Cl} > \text{NaCN} > \text{NaCl} > \text{HCl}$

21. The degree of hydrolysis of a salt of W_4 and W_8 in its 0.1 M solution is 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt would be

- (1) 25%
- (2) 50%
- (3) 75%
- (4) 100%

22. pH of separate solution of four potassium salts, KW, KX, KY, and KZ are 7.0, 9.0, 10.0, and 10.5, respectively. If each solution is 0.2 M, the strongest acid would be

- (1) HW
- (2) HX
- (3) HY
- (4) HZ

23. Which of the following solutions have $\text{pH} < 7$.

- (1) BaI_2
- (2) $\text{Al}(\text{NO}_3)_3$
- (3) $\text{CH}_3\text{COONH}_4$
- (4) CsI

24. Which of the following solution have $\text{pH} > 7$.

- I. BaF_2
- II. RbI

III. C_6H_5COONa

(1) I

(3) I, III

IV. $(CH_3COO)_2Ba$

(2) I, II, III

(4) I, III, IV

25. The expression to calculate pH of sodium acetate solution at $25^\circ C$ is

(1) $pH = 7 + \frac{1}{2} pK_b (CH_3COOH) - \frac{1}{2} \log [\text{salt}]$

(2) $pH = 7 + \frac{1}{2} pK_a (CH_3COOH) - \frac{1}{2} \log [\text{salt}]$

(3) $pH = 7 + \frac{1}{2} pK_b (CH_3COOH) + \frac{1}{2} \log [\text{salt}]$

(4) $pH = 7 + \frac{1}{2} pK_a (CH_3COOH) + \frac{1}{2} \log [\text{salt}]$

26. The correct order of increasing $[H_3O^+]$ in the following aqueous solution is

(1) $0.01 \text{ M } H_2S < 0.01 \text{ M } H_2SO_4 < 0.01 \text{ M } NaCl < 0.01 \text{ M } NaNO_3$

(2) $0.01 \text{ M } NaCl = 0.01 \text{ M } NaNO_3 < 0.01 \text{ M } H_2S < 0.01 \text{ M } H_2SO_4$

(3) $0.01 \text{ M } H_2S < 0.01 \text{ M } NaNO_3 = 0.01 \text{ M } NaCl < 0.01 \text{ M } H_2SO_4$

(4) $0.01 \text{ M } H_2S < 0.01 \text{ M } NaNO_3 < 0.01 \text{ M } NaCl < 0.01 \text{ M } H_2SO_4$

27. pH of water is 7. When a substance Y is dissolved in water, the pH becomes 11. The substance Y is a salt of

(1) Weak acid and weak base

(2) Strong acid and strong base

(3) Strong acid and weak base

(4) Weak acid and strong base

28. The hydrolysis constant of 0.1 M aqueous solution of sodium acetate if K_a of $CH_3COOH = 1.8 \times 10^{-5}$ is

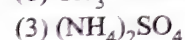
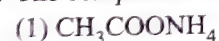
(1) 5.5×10^{-10}

(2) 4.5×10^{-8}

(3) 5.5×10^{-12}

(4) None of these

29. The compound whose 0.1 M solution is basic is

30. K_a for ascorbic acid ($HASc$) is 5×10^{-5} . Calculate the $[H^+]$ in an aqueous solution in which the concentration of ASc^- ions is 0.02 M.

(1) 2×10^{-6}

(2) 2×10^{-7}

(3) 5×10^{-9}

(4) 5×10^{-10}

ANSWERS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (4) | 2. (1) | 3. (3) | 4. (2) | 5. (2) |
| 6. (2) | 7. (3) | 8. (1) | 9. (4) | 10. (3) |
| 11. (1) | 12. (3) | 13. (4) | 14. (4) | 15. (4) |
| 16. (1) | 17. (1) | 18. (1) | 19. (2) | 20. (3) |
| 21. (2) | 22. (1) | 23. (2) | 24. (4) | 25. (4) |
| 26. (2) | 27. (4) | 28. (1) | 29. (4) | 30. (3) |

8.17 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

Solubility of ionic solids in water is very high. Some of these are so soluble that they are hygroscopic in nature and even absorb water vapours from the atmosphere. Others have so little solubility that these are called insoluble. The solubility depends on the lattice energy of the salt and the hydration of ions in the aqueous solutions (i.e. hydration energy). Each salt has its characteristic solubility and depends on temperature. Such salts are classified on the basis of their solubility in the following three categories.

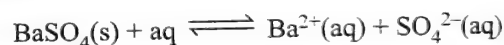
Category I	Soluble	Solubility $> 0.1 \text{ M}$
Category II	Slightly soluble	Solubility $< 0.1 \text{ M}$
Category III	Sparingly soluble	Solubility $< 0.01 \text{ M}$

8.17.1 SOLUBILITY PRODUCT CONSTANT

Certain salts, such as $AgCl$, $BaSO_4$, Ag_2S and PbS , are considered as insoluble in water. Actually no insoluble salt is actually completely insoluble, they have a very small solubility. Such salts are called sparingly soluble salts.

Some of them are: Ag_2SO_4 , Ag_2CO_3 , $PbCl_2$, $PbCrO_4$, PbS , ZnS , $Al(OH)_3$, $Ca_3(PO_4)_2$, $CaSO_4$, MnS , $Zr_3(PO_4)_4$

Consider a solid such as $BaSO_4$ in contact with its saturated aqueous solution. If the dissociation process is represented by the equation:



Then, the equilibrium constant is given by the equation

$$K = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]} \quad \dots(i)$$

For a pure solid substance, the concentration remains constant and equation (i) becomes

$$K[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] \quad \dots(ii)$$

K_{sp} is called the solubility product constant or simply solubility product.

Thus, solubility product of an electrolyte at a specified temperature is defined as the product of the molar concentration of its ions in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

The experimental value of K_{sp} in equation (ii) at 298 K is 1.1×10^{-10} . This means that for solid $BaSO_4$ in equilibrium with its saturated solution, the product of the concentration of Ba^{2+} and SO_4^{2-} ions is equal to its solubility product constant. The concentration of the two ions will be equal to the molar solubility of $BaSO_4$. If molar solubility is S , then

$$K_{sp} = (S)(S) = S^2 = 1.1 \times 10^{-10}$$

$$\therefore S = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5} \text{ mol L}^{-1}$$

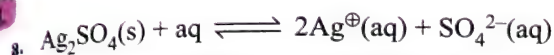
Therefore, K_{sp} is expressed in concentration units. The reaction coefficients Q in such system is known as ionic product.

Note: The solubility of a salt in water depends upon other substances (ions) present in water (at that time). The solubility product is a constant value (at a given temperature) and is independent of the presence of any other ion present. Like other equilibrium constants, such as K_p , K_c , K_a , and K_b , it is also a constant at a certain temperature and changes only when the temperature changes.

ILLUSTRATION 8.102

Calculate the solubilities of the following.

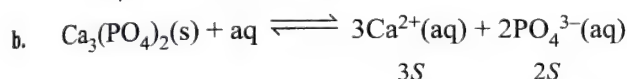
- a. Ag_2SO_4 b. $\text{Ca}_3(\text{PO}_4)_2$
c. $[\text{Zr}_3(\text{PO}_4)_4]$ d. K_{sp} for $\text{M}_x\text{X}_y(\text{s})$



If the molar solubility of the solid substance is S mol L^{-1} , then

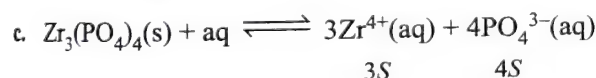
$$K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (2S)^2 (S) = 2^2 \cdot 1^1 \cdot S^3 = 4S^3 \text{ M}^3$$

$$\text{or } S = \sqrt[3]{\frac{K_{sp}}{4}} \text{ or } \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} \text{ M}$$



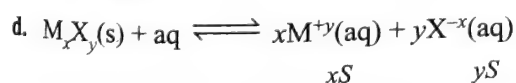
$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3S)^3 (2S)^2 = 3^3 \cdot 2^2 \cdot S^5 = 108S^5 \text{ M}^5$$

$$\text{or } S = \sqrt[5]{\frac{K_{sp}}{108}} \text{ M or } (K_{sp}/108)^{\frac{1}{5}} \text{ M}$$



$$K_{sp} = [\text{Zr}^{4+}]^3 [\text{PO}_4^{3-}]^4 = (3S)^3 (4S)^4 = 3^3 \cdot 4^4 \cdot S^7 = 6912S^7 \text{ M}^7$$

$$\text{or } S = \left(\frac{K_{sp}}{6912}\right)^{\frac{1}{7}}$$



$$K_{sp} = [\text{M}^{+y}]^x [\text{X}^{-x}]^y = (xS)^x (yS)^y = x^x \cdot y^y \cdot S^{x+y} \text{ M}^{(x+y)} \quad \dots(i)$$

$$\text{or } S^{(x+y)} = \frac{K_{sp}}{x^x \cdot y^y}$$

$$S = \left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{\frac{1}{x+y}}$$

e. Relation between K_{sp} and molar solubility of a sparingly soluble salt:

Type of salt	Relation between S and K_{sp}	Units
MX	$K_{sp} = S^2$	M^2 or $(\text{M/L})^2$ or $(\text{mol dm}^{-3})^2$
MX_2	$K_{sp} = 1^1 \cdot 2^2 \cdot S^3 = 4S^3$	M^3 or $(\text{M/L})^3$ or $(\text{mol dm}^{-3})^3$
MX_3	$K_{sp} = 1^1 \cdot 3^3 \cdot S^4 = 27S^4$	M^4 or $(\text{M/L})^4$ or $(\text{mol dm}^{-3})^4$
MX_4	$K_{sp} = 1^1 \cdot 4^4 \cdot S^5 = 256S^5$	M^5 or $(\text{M/L})^5$ or $(\text{mol dm}^{-3})^5$
M_2X_3	$K_{sp} = 2^2 \cdot 3^3 \cdot S^5 = 108S^5$	M^5 or $(\text{M/L})^5$ or $(\text{mol dm}^{-3})^5$
M_xX_y	$K_{sp} = x^x \cdot y^y \cdot (S)^{x+y}$	M^{x+y} or $(\text{M L}^{-1})^{x+y}$ or $(\text{mol dm}^{-3})^{x+y}$

The term K_{sp} in eq (ii) is given the symbol Q_{sp} , when the concentrations of one or more species are not the concentrations under equilibrium. Under equilibrium conditions, $K_{sp} = Q_{sp}$, but otherwise it gives the direction of the processes of precipitation or dissolution.

Table 8.10 The solubility product constants K_{sp} of some common ionic salts at 298 K

Name of the Salt	Formula	K_{sp}
Silver bromide	AgBr	5.0×10^{-13}
Silver carbonate	Ag_2CO_3	8.1×10^{-12}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Silver chloride	AgCl	1.8×10^{-10}
Silver iodide	AgI	8.3×10^{-17}
Silver sulphate	Ag_2SO_4	1.4×10^{-5}
Aluminium hydroxide	$\text{Al}(\text{OH})_3$	1.3×10^{-33}
Barium chromate	BaCrO_4	1.2×10^{-10}
Barium fluoride	BaF_2	1.0×10^{-6}
Barium sulphate	BaSO_4	1.1×10^{-10}
Calcium carbonate	CaCO_3	2.8×10^{-9}
Calcium fluoride	CaF_2	5.3×10^{-9}
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	5.5×10^{-6}
Calcium oxalate	CaC_2O_4	4.0×10^{-9}
Calcium sulphate	CaSO_4	9.1×10^{-6}
Cadmium hydroxide	$\text{Cd}(\text{OH})_2$	2.5×10^{-14}
Cadmium sulphide	CdS	8.0×10^{-27}
Chromic hydroxide	$\text{Cr}(\text{OH})_3$	6.3×10^{-31}
Cuprous bromide	CuBr	5.3×10^{-9}
Cupric carbonate	CuCO_3	1.4×10^{-10}
Cuprous chloride	CuCl	1.7×10^{-6}
Cupric hydroxide	$\text{Cu}(\text{OH})_2$	2.2×10^{-20}
Cuprous iodide	CuI	1.1×10^{-12}
Cupric sulphide	CuS	6.3×10^{-36}
Ferrous carbonate	FeCO_3	3.2×10^{-11}
Ferrous hydroxide	$\text{Fe}(\text{OH})_2$	8.0×10^{-16}
Ferric hydroxide	$\text{Fe}(\text{OH})_3$	1.0×10^{-38}
Ferrous sulphide	FeS	6.3×10^{-18}
Mercurous bromide	Hg_2Br_2	5.6×10^{-23}
Mercurous chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous iodide	Hg_2I_2	4.5×10^{-29}
Mercurous sulphate	Hg_2SO_4	7.4×10^{-7}
Mercuric sulphide	HgS	4.0×10^{-53}

Magnesium carbonate	MgCO ₃	3.5×10^{-8}
Magnesium fluoride	MgF ₂	6.5×10^{-9}
Magnesium hydroxide	Mg(OH) ₂	1.8×10^{-11}
Magnesium oxalate	MgC ₂ O ₄	7.0×10^{-7}
Manganese carbonate	MnCO ₃	1.8×10^{-11}
Manganese sulphide	MnS	2.5×10^{-13}
Nickel hydroxide	Ni(OH) ₂	2.0×10^{-15}
Nickel sulphide	NiS	4.7×10^{-5}
Lead bromide	PbBr ₂	4.0×10^{-5}
Lead carbonate	PbCO ₃	7.4×10^{-14}
Lead chloride	PbCl ₂	1.6×10^{-5}
Lead fluoride	PbF ₂	7.7×10^{-8}
Lead hydroxide	Pb(OH) ₂	1.2×10^{-15}
Lead iodide	PbI ₂	7.1×10^{-9}
Lead sulphate	PbSO ₄	1.6×10^{-8}
Lead sulphide	PbS	8.0×10^{-28}
Stannous hydroxide	Sn(OH) ₂	1.4×10^{-28}
Stannous sulphide	SnS	1.0×10^{-25}
Strontium carbonate	SrCO ₃	1.1×10^{-10}
Strontium fluoride	SrF ₂	2.5×10^{-9}
Strontium sulphate	SrSO ₄	3.2×10^{-7}
Thallous bromide	TlBr	3.4×10^{-6}
Thallous chloride	TlCl	1.7×10^{-4}
Thallous iodide	TlI	6.5×10^{-8}
Zinc carbonate	ZnCO ₃	1.4×10^{-11}
Zinc hydroxide	Zn(OH) ₂	1.0×10^{-15}
Zinc sulphide	ZnS	1.6×10^{-24}

8.17.2 DIFFERENCE BETWEEN SOLUBILITY PRODUCT AND IONIC PRODUCT

Both the terms represent the product of the concentrations of the ions in the solution, each raised to the power equal to the number of ions as represented by the dissociation of one molecule of the substance. But they differ in the following two aspects:

- a. Ionic product is applicable to all types of solution, saturated or unsaturated.

Whereas solubility product is applicable only to saturated solutions in which there exists a dynamic equilibrium between the undissolved salt and the ions present in solution. Therefore, the solubility product is, in fact, the ionic product for a saturated solution.

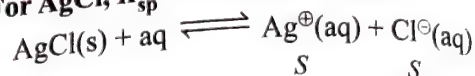
- b. The solubility product of a salt is constant at constant temperature whereas ionic product depends upon the concentrations of ions in the solution.

ILLUSTRATION 8.103

Determine the solubility of (a) AgCl, (b) Fe(OH)₃, (c) Hg₂Br₂, and (d) Ag₂SO₄ from their solubility product constants given in table 8.9. Calculate the molarities of the individual ions and also the solubilities of salts in g L⁻¹.

Sol.

- a. For AgCl, $K_{sp} = 1.8 \times 10^{-10}$, hence



$$K_{sp} = [\text{Ag}^{\oplus}] [\text{Cl}^{\ominus}]$$

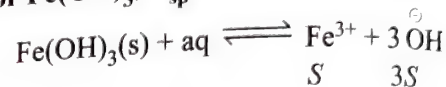
$$K_{sp} = S^2 M^2$$

i. $S/M = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5}$

$[\text{Ag}^{\oplus}] = [\text{Cl}^{\ominus}]; S = 1.34 \times 10^{-5} \text{ mol L}^{-1}$

ii. S of AgCl in g L⁻¹ = $1.34 \times 10^{-5} \times 143.35 \text{ g mol}^{-1}$
= $1.92 \times 10^{-3} \text{ g L}^{-1}$

- b. For Fe(OH)₃, $K_{sp} = 1.0 \times 10^{-38}$, hence



$$\therefore K_{sp} = [\text{Fe}^{3+}] [\text{OH}^{\ominus}]^3 = S \cdot (3S)^3 = 1^1 \cdot 3^3 S^4 = 27 S^4 M^4$$

i. $S/M = \left(\frac{1.0 \times 10^{-38}}{27} \right)^{1/4}; S = 1.39 \times 10^{-10}$

ii. $[\text{Fe}^{3+}] = S = 1.39 \times 10^{-10} \text{ mol L}^{-1}$

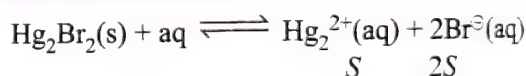
$[\text{OH}^{\ominus}] = 3S = 3 \times 1.39 \times 10^{-10}$
= $4.17 \times 10^{-10} \text{ mol L}^{-1}$

iii. S for Fe(OH)₃ in g L⁻¹

$S = 1.39 \times 10^{-10} \text{ mol L}^{-1} \times 106.85 \text{ g mol}^{-1}$
= $1.40 \times 10^{-8} \text{ g L}^{-1}$

- c. For Hg₂Br₂, $K_{sp} = 5.6 \times 10^{-23}$, hence

Note: Mercurous ion exist as Hg₂²⁺.



$$K_{sp} = [\text{Hg}_2^{2+}] [\text{Br}^{\ominus}]^2$$

$$= (S) (2S)^2 = 1^1 \cdot 2^2 \cdot S^3 = 4 S^3 \cdot M^3$$

i. $S/M = \left(\frac{5.6 \times 10^{-23}}{4} \right)^{1/3}; S = 2.41 \times 10^{-8} \text{ mol L}^{-1}$

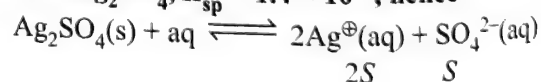
ii. and S for Hg₂Br₂ in g L⁻¹

$S = 2.41 \times 10^{-8} \text{ mol L}^{-1} \times 360.4 \text{ g mol}^{-1}$
= $8.68 \times 10^{-6} \text{ g L}^{-1}$

iii. $[\text{Hg}_2^{2+}] = 2.41 \times 10^{-8} \text{ M}$,

$[\text{Br}^{\ominus}] = 2 \times 2.41 \times 10^{-8} \text{ M} = 4.82 \times 10^{-8} \text{ M}$

- d. For Ag₂SO₄, $K_{sp} = 1.4 \times 10^{-5}$, hence



$$K_{sp} = [\text{Ag}^{\oplus}]^2 [\text{SO}_4^{2-}]$$

$$= (2S)^2 (S) = 2^2 \cdot 1^1 \cdot S^3 \text{ M}^3 = 4 S^3 M^3$$

i. $S/M = \left(\frac{1.4 \times 10^{-5}}{4} \right)^{1/3}; S = 1.52 \times 10^{-2} \text{ mol L}^{-1}$

ii. and S for Ag₂SO₄ in g L⁻¹

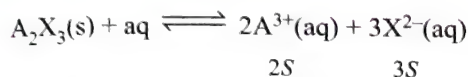
$S = 1.52 \times 10^{-2} \text{ mol L}^{-1} \times 311.8 \text{ g mol}^{-1}$
= 4.74 g L^{-1}

$$\begin{aligned}\text{iii. } [\text{Ag}^{\oplus}] &= 2S = 2 \times 1.52 \times 10^{-2} \\ &= 3.04 \times 10^{-2} \text{ mol L}^{-1} \\ [\text{SO}_4^{2-}] &= S = 1.52 \times 10^{-2} \text{ mol L}^{-1}\end{aligned}$$

ILLUSTRATION 8.104

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with H_2O . The solubility product of A_2X_3 , $K_{\text{sp}} = 1.1 \times 10^{-23}$.

Sol. If S is the solubility of A_2X_3 ,



$$\therefore [\text{A}^{3+}] = 2S, [\text{X}^{2-}] = 3S$$

$$\text{Therefore, } K_{\text{sp}} = (2S)^2 (3S)^3 = 108S^5 = 1.1 \times 10^{-23}$$

$$\text{Thus, } S^5 = 1 \times 10^{-25}$$

$$S = 1.0 \times 10^{-5} \text{ mol L}^{-1}$$

ILLUSTRATION 8.105

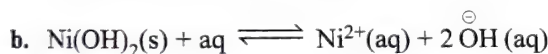
The values of K_{sp} of two sparingly soluble salts, $\text{Ni}(\text{OH})_2$ and AgCN are 2.0×10^{-15} and 6×10^{-7} respectively, which salt is more soluble? Explain.



$$K_{\text{sp}} = [\text{Ag}^{\oplus}] [\text{CN}^{\ominus}] = 6 \times 10^{-17}$$

$$\text{Let } [\text{Ag}^{\oplus}] = S_1, \text{ then } [\text{CN}^{\ominus}] = S_1$$

$$\therefore S_1^2 = 6 \times 10^{-17}; S_1 = 7.8 \times 10^{-9}$$



$$\text{Let } [\text{Ni}^{2+}] = S_2, \text{ then } [\text{OH}^{\ominus}] = 2S_2$$

$$\therefore (S_2) (2S_2)^2 = 2 \times 10^{-15}$$

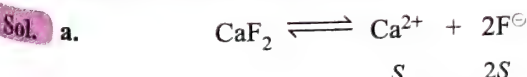
$$\therefore S_2 = 0.58 \times 10^{-4}$$

Therefore, $\text{Ni}(\text{OH})_2$ is more soluble than AgCN .

ILLUSTRATION 8.106

Calculation of K_{sp} when concentration of one of the ions is given.

- A solution of CaF_2 is found to contain $10^{-4} \text{ M F}^{\ominus}$ ions. What is the K_{sp} of CaF_2 ?
- A solution of calcium phosphate contains $2 \times 10^{-5} \text{ M PO}_4^{3-}$ ions. What is K_{sp} of $\text{Ca}_3(\text{PO}_4)_2$?
- A solution of $\text{Ca}_3(\text{PO}_4)_2$ contains $6 \times 10^{-5} \text{ M Ca}^{2+}$ ions. What is the K_{sp} of $\text{Ca}_3(\text{PO}_4)_2$?
- A solution of $\text{Zr}_3(\text{PO}_4)_4$ contains $8 \times 10^{-5} \text{ M PO}_4^{3-}$ ions. What is the K_{sp} of $\text{Zr}_3(\text{PO}_4)_4$?
- A solution of $\text{Zr}_3(\text{PO}_4)_4$ contains $3 \times 10^{-5} \text{ M Zr}^{4+}$ ions. What is the K_{sp} of $\text{Zr}_3(\text{PO}_4)_4$?



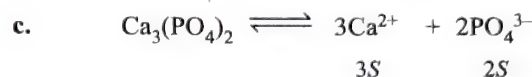
$$\text{Total } [\text{F}^{\ominus}] = 2S = 10^{-4}, S = \left(\frac{10^{-4}}{2}\right) \text{ M}$$

$$K_{\text{sp}} = 4S^3 = 4 \times \left(\frac{10^{-4}}{2}\right)^3 = 0.5 \times 10^{-12} \text{ M}^3$$



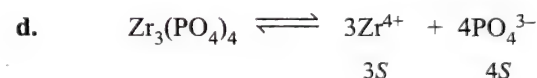
$$\text{Total } [\text{PO}_4^{3-}] = 2S = 2 \times 10^{-5} \text{ M}; S = 10^{-5} \text{ M}$$

$$\begin{aligned}K_{\text{sp}} &= 3^3 \cdot 2^2 \cdot S^5 = 108S^5 = 108 \times (10^{-5})^5 \\ &= 108 \times 10^{-25} \text{ M}^5 \\ &= 1.08 \times 10^{-23}\end{aligned}$$



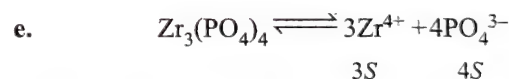
$$\text{Total } [\text{Ca}^{2+}] = 3S = 6 \times 10^{-5} \text{ M}; S = 2 \times 10^{-5} \text{ M}$$

$$\begin{aligned}K_{\text{sp}} &= 108S^5 = 108 \times (2 \times 10^{-5})^5 = 108 \times 32 \times 10^{-25} \\ &= 3456 \times 10^{-25} \\ &= 34.56 \times 10^{-23} \text{ M}^5 \\ &= 3.456 \times 10^{-22} \text{ M}^5\end{aligned}$$



$$\text{Total } [\text{PO}_4^{3-}] = 4S = 8 \times 10^{-5} \text{ M}; S = 2 \times 10^{-5} \text{ M}$$

$$\begin{aligned}K_{\text{sp}} &= 3^3 \cdot 4^4 \cdot S^7 = 6912S^7 = 6912 (2 \times 10^{-5})^7 \\ &= 6912 \times 128 \times 10^{-35} \\ &= 884736 \times 10^{-35} \\ &= 8.85 \times 10^{-30} \text{ M}^7\end{aligned}$$



$$\text{Total } [\text{Zr}^{4+}] = 3S = 3 \times 10^{-5} \text{ M}; S = 10^{-5} \text{ M}$$

$$\begin{aligned}K_{\text{sp}} &= 6912S^7 = 6912 (10^{-5})^7 = 6912 \times 10^{-35} \text{ M}^7 \\ &= 69.12 \times 10^{-33} \text{ M}^7 \\ &= 6.912 \times 10^{-32} \text{ M}^7\end{aligned}$$

8.18 COMMON ION EFFECT ON SOLUBILITY OF IONIC SALTS

According to Le Chatelier's principle, if the concentration of any one of the ions is increased, it should combine with ion of its opposite charge and some of the salt will be precipitated till $K_{\text{sp}} = Q_{\text{sp}}$.

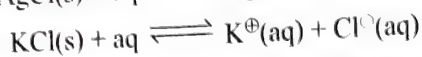
Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $K_{\text{sp}} = Q_{\text{sp}}$. It is applicable even to soluble salts such as NaCl except that due to higher concentration of the ions, instead of their molarities, their activities are used in the expression for Q_{sp} .

Alternatively:

If to an ionic equilibrium $\text{XY} \rightleftharpoons \text{X}^{\oplus} + \text{Y}^{\ominus}$, a salt containing a common ion (XA or YB) is added, the equilibrium shifts in the backward direction. This is called *common ion effect*.

For example

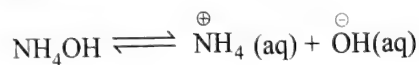
- a. To the solution of AgCl in H₂O (being a saturated solution because solubility of AgCl in H₂O is very small), if KCl is added which provides the common Cl[⊖] ions, the solubility of AgCl decreases.



According to Le Chatelier's principle, increase in [Cl[⊖]] shifts the equilibrium in the backward direction, i.e., some solid AgCl precipitates out.

Note: K_{sp} of a salt is constant irrespective of the source of ions, the solubility of a sparingly soluble salt in the presence of a soluble salt having common ion can be calculated.

- b. To the solution of a weak base NH₄OH, if NH₄Cl is added which provides common NH₄[⊕] ions, the ionisation of NH₄OH is suppressed.



Thus, 'common ion effect' is defined as follows: *If to the solution of a weak electrolyte (e.g., CH₃COOH or NH₃ or NH₄OH) which ionises to small extent, a strong electrolyte having a common ion is added which ionises completely, the ionisation of weak electrolyte is further suppressed.*

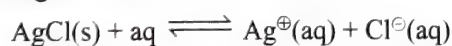
8.18.1 CALCULATION OF NEW SOLUBILITY AFTER ADDITION OF COMMON ION

- a. For uni-univalent or bi-bivalent sparingly soluble salt

(e.g., AgCl and BaSO₄), and the common ion is either cation (Ag[⊕]) or anion (Cl[⊖]) or Ba²⁺ or SO₄²⁻ ion.

Let 0.1 M NaCl is added to the solution of AgCl.

$$K_{sp} \text{ of AgCl} = 1.8 \times 10^{-10}$$



Let S is the solubility of AgCl. Dissolution of S mol L⁻¹ of AgCl provides S mol L⁻¹ of Ag[⊕] and S mol L⁻¹ of Cl[⊖] ions. But total concentration of Cl[⊖] = $(0.1 + S)$ mol L⁻¹ because the solution already contains 0.1 M of Cl[⊖] ions from NaCl (which is completely ionised).

$$K_{sp} = 1.8 \times 10^{-10} = [\text{Ag}^{\oplus}] [\text{Cl}^{\ominus}] = (S) (0.1 + S)$$

As K_{sp} is small, $S \ll 0.1$ M

$$\text{Thus, } (0.1 + S) \approx 0.1$$

$$\text{Hence, } 1.8 \times 10^{-10} = S(0.1)$$

$$S = \frac{1.8 \times 10^{-10}}{0.1} = 1.8 \times 10^{-9} \text{ M}$$

$$S_{\text{new}} = \frac{K_{sp}}{C}$$

(where C is the concentration of common ion added)

$$S_{\text{initial}} = (K_{sp})^{1/2} [\because K_{sp} = S^2]$$

- b. For bi-univalent sparingly soluble salt [e.g., Ni(OH)₂], and the common ion is anion (OH[⊖]):

Let 0.1 M NaOH is added to the solution of Ni(OH)₂.

$$K_{sp} \text{ of Ni(OH)}_2 = 2.0 \times 10^{-15}$$

Let S is the solubility of Ni(OH)₂. The dissolution of S mol L⁻¹ of Ni(OH)₂ provides S mol L⁻¹ of Ni²⁺ and

$2S$ mol L⁻¹ of OH[⊖] ions, but the total concentration of

OH[⊖] = $(0.10 + 2S)$ mol L⁻¹ because the solution already

contains 0.10 mol L⁻¹ of OH[⊖] ions from NaOH.

$$K_{sp} = 2.0 \times 10^{-15} = [\text{Ni}^{2+}] [\text{OH}^{\ominus}]^2 = (S) (0.10 + 2S)^2$$

As K_{sp} is small, $2S \ll 0.10$.

$$\text{Thus, } (0.10 + 2S) \approx 0.10$$

Hence,

$$2.0 \times 10^{-15} = S(0.10)^2$$

$$S = \frac{2.0 \times 10^{-15}}{(0.10)^2} = 2.0 \times 10^{-13} \text{ M}$$

$$\therefore S_{\text{new}} = \frac{K_{sp}}{(C)^2}$$

(C = concentration of the common ion added)

$$S_{\text{initial}} = \left(\frac{K_{sp}}{4} \right)^{1/3} (\because K_{sp} = 4S^3)$$

- c. For bi-univalent sparingly soluble salt (e.g. Ni(OH)₂), and the common ion is cation (e.g. Ni²⁺):

Let 0.1 M NiCl₂ is added, to the solution of Ni(OH)₂. In this case, common ion is Ni²⁺ ion.

$$\therefore K_{sp} = 2.0 \times 10^{-15} = [\text{Ni}^{2+}] [\text{OH}^{\ominus}]^2 = (S + 0.1) (2S)^2$$

As K_{sp} is small, $S \ll 0.10$

$$\text{Thus, } (S + 0.1) \approx 0.1$$

$$\text{Hence, } 2.0 \times 10^{-15} = 0.1 \times 4S^2$$

$$S_{\text{new}} = \left(\frac{2.0 \times 10^{-15}}{0.1 \times 4} \right)^{1/2}$$

$$S_{\text{new}} = \left(\frac{K_{sp}}{4 \times C} \right)^{1/2} \left[\text{where } C \text{ is the concentration of the common ion added} \right]$$

$$S_{\text{initial}} = \left(\frac{K_{sp}}{4} \right)^{1/3}$$

- d. For tri-univalent sparingly soluble salt (e.g. Al(OH)₃), and the common ion is anion (OH[⊖]):

Let 0.1 M NaOH is added to the solution of Al(OH)₃:

$$(K_{sp} \text{ of Al(OH)}_3 = 1.3 \times 10^{-33})$$

$$\therefore K_{sp} = 1.3 \times 10^{-33} = [\text{Al}^{3+}] [\text{OH}^{\ominus}]^3 = (S) (3S + 0.1)^3$$

As K_{sp} is very small, $3S \ll 0.1$

Thus, $(0.1 + 3S) \approx 0.1$

Hence, $1.3 \times 10^{-33} = (S)(0.10)^3$

$$S_{\text{new}} = \frac{1.3 \times 10^{-33}}{(0.10)^3} = 1.3 \times 10^{-30}$$

$$S_{\text{new}} = \frac{K_{sp}}{(C)^3} \quad \left(\text{where } C \text{ is the concentration of the common ion added} \right)$$

$$S_{\text{initial}} = \left(\frac{K_{sp}}{27} \right)^{1/4} \quad (\because K_{sp} = 27S^4)$$

e. For tri-univalent sparingly soluble salt (e.g., $\text{Al}(\text{OH})_3$),
and the common ion is cation (Al^{3+}):

Let 0.1 M AlI_3 (assuming AlI_3 completely ionised) is added to the solution of $\text{Al}(\text{OH})_3$.
In this case, Al^{3+} is the common ion.

$$K_{sp} = 1.3 \times 10^{-33} = [\text{Al}^{3+}] [\text{OH}^-]^3$$

$$= (S + 0.1) (3S)^3 \quad (\because S + 0.1 \approx 0.1)$$

$$\approx (0.1) (3S)^3$$

$$\therefore S_{\text{new}} = \left(\frac{1.3 \times 10^{-33}}{0.1 \times 27} \right)^{1/3}$$

$$\therefore S_{\text{new}} = \left(\frac{K_{sp}}{27 \times C} \right)^{1/3} \quad \left[\text{where } C \text{ is the concentration of the common ion added} \right]$$

$$S_{\text{initial}} = \left(\frac{K_{sp}}{27} \right)^{1/4} \quad (\because K_{sp} = 27S^4)$$

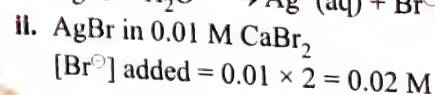
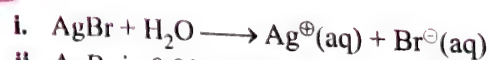
Table 8.11 Solubility of a sparingly soluble salt in presence of common ion (when K_{sp} is very small)

Types of sparingly soluble salt	Common ion added	S in H_2O (Solubility) (S_{initial})	S is common ion. (S_{new})
a. For uni-univalent type (e.g., AgCl) or For bi-bivalent type (e.g. BaSO_4)	Either cation or anion (e.g., Ag^+ or Cl^-) or Ba^{2+} ion or SO_4^{2-} ion	$K_{sp} = S^2$ $S_{\text{H}_2\text{O}} = (K_{sp})^{1/2}$	$S_{\text{new}} = K_{sp}/(C)^n$ $C = \text{concentration of common ion added.}$ $n = \text{number of common ion in sparingly soluble salts.}$
b. For bi-univalent type e.g., $\text{Ni}(\text{OH})_2$	Anion (OH^- ion)	$K_{sp} = 4S^3$ $S_{\text{H}_2\text{O}} = \left(\frac{K_{sp}}{4} \right)^{1/3}$	$S_{\text{new}} = \frac{K_{sp}}{(C)^n} = \frac{K_{sp}}{(C)^2}$
	Cation (Ni^{2+} ion)		$S_{\text{new}} = \left(\frac{K_{sp}}{4 \times C} \right)^{1/2}$
c. For uni-bivalent type e.g., $\text{Ag}_2\text{C}_2\text{O}_4$	Cation (Ag^+ ion)	$S_{\text{H}_2\text{O}} = \left(\frac{K_{sp}}{4} \right)^{1/3}$	$S_{\text{new}} = \frac{K_{sp}}{(C)^n} = \frac{K_{sp}}{(C)^2}$
	Anion ($\text{C}_2\text{O}_4^{2-}$ ion)		$S_{\text{new}} = \left(\frac{K_{sp}}{4 \times C} \right)^{1/2}$
d. For tri-univalent type e.g., $\text{Al}(\text{OH})_3$	Anion (OH^- ion)	$K_{sp} = 27S^4$ $S_{\text{H}_2\text{O}} = \left(\frac{K_{sp}}{27} \right)^{1/4}$	$S_{\text{new}} = \frac{K_{sp}}{(C)^n} = \frac{K_{sp}}{(C)^3}$
	Cation (Al^{3+} ion)		$S_{\text{new}} = \left(\frac{K_{sp}}{27 \times C} \right)^{1/3}$

ILLUSTRATION 8.107

Let the solubilities of AgBr in water and in 0.01 M CaBr_2 , 0.01 M KBr , and 0.05 M AgNO_3 be S_1 , S_2 , S_3 and S_4 , respectively. Give the decreasing order of the solubilities.

Sol.



iii. AgBr in 0.01 M KBr

... S_3

[Br[⊖]] added = 0.01 M

iv. AgBr in 0.05 M AgNO₃

... S_4

[Ag[⊕]] added = 0.05 M

Since both Br[⊖] ions and Ag[⊕] ions act as common ions, so larger the concentration of Br[⊖] or Ag[⊕] ion added, more is the suppression of ionisation of AgBr and hence less will be the solubility of AgBr.

Therefore, the decreasing solubility order:

$$S_1 > S_3 > S_2 > S_4$$

ILLUSTRATION 8.108

The K_{sp} of AgCl at 25°C is 1.5×10^{-10} . Find the solubility (in g L⁻¹) in an aqueous solution containing 0.01 M AgNO₃.

Sol. AgNO₃ is completely ionised. Due to common ion (Ag[⊕]), the dissociation of AgCl is suppressed and hence, the solubility decreases.

Since K_{sp} is small, $S \ll 0.01$ M.

Thus, $(0.01 + S) \approx 0.01$.

[For uni-univalent salt]

$$\begin{aligned} S_{\text{new}} &= \frac{K_{sp}}{(C)^n} = \frac{1.5 \times 10^{-10}}{(0.01)^1} = 1.5 \times 10^{-8} \text{ M} \\ &= 1.5 \times 10^{-8} \times 143.5 \\ &= 2.15 \times 10^{-6} \text{ g L}^{-1} \end{aligned}$$

The solubility of AgCl in water containing Ag[⊕] (a common ion) is much less than that in pure water.

ILLUSTRATION 8.109

Calculate the molar solubility of Ni(OH)₂ in 0.10 M NaOH. The ionic product of Ni(OH)₂ is 2.0×10^{-15} .

Sol. First Method:

For bi-univalent type, e.g., Ni(OH)₂

$$k_{sp} = 4s^3 S_{\text{H}_2\text{O}} = \left(\frac{k_{sp}}{4}\right)^{1/3}$$

$$S_{\text{new}} = \frac{k_{sp}}{[\text{OH}^\ominus]^2} = \frac{2.0 \times 10^{-15}}{(0.10)^2} = 2.0 \times 10^{-3} \text{ M}$$

$$\therefore [\text{Ni}^{2+}] = 2.0 \times 10^{-3} \text{ M}$$

Second Method:

Let the solubility of Ni(OH)₂ be S. Dissolution of S mol. L⁻¹

of Ni(OH)₂ provides S mol L⁻¹ and 2S mol⁻¹ of [OH[⊖]] ions

but the total concentration of [OH[⊖]] = (0.10 + 2S) mol. L⁻¹ because the solution already contains 0.1 mol. L⁻¹ from NaOH.

$$\begin{aligned} \therefore k_{sp} &= 2.0 \times 10^{-15} = [\text{Ni}^{2+}] [\text{OH}^\ominus]^2 \\ &= (S) (0.10 + 2S)^2 \end{aligned}$$

As k_{sp} is small,

$$2S \ll 0.10$$

Thus $(0.10 + 2S) \approx 0.10$

Hence,

$$\begin{aligned} 2.0 \times 10^{-15} &= S(0.10)^2 \\ S &= 2.0 \times 10^{-13} \text{ M} = [\text{Ni}^{2+}] \end{aligned}$$

ILLUSTRATION 8.110

The solubility of BaSO₄ in water is 2.33 g 100 mL⁻¹. Calculate the percentage loss in weight when 0.2 g of BaSO₄ is washed with

a. 1 L of water

b. 1 L of 0.01 N H₂SO₄ [$M_{w_{\text{BaSO}_4}} = 233 \text{ g mol}^{-1}$]

Sol.

a. Solubility is in general expressed in g L⁻¹, so solubility of BaSO₄ = $2.33 \times 10^{-3} \text{ g L}^{-1}$.

Loss in weight of BaSO₄ = Amount of BaSO₄ soluble.

$$\Rightarrow \% \text{ loss} = \frac{2.33 \times 10^{-3}}{0.2} \times 100 = 1.16\%$$

b. 0.01 N H₂SO₄ \equiv 0.01 N SO₄²⁻ ions

$$\equiv 0.005 \text{ M SO}_4^{2-} \text{ ions}$$

(n factor for SO₄²⁻ = 2)

Now presence of SO₄²⁻ prior to washing BaSO₄ will suppress the solubility of BaSO₄ (due to common ion effect). The suppression will be governed by K_{sp} value of BaSO₄. So, first calculate the K_{sp} of BaSO₄.

Solubility of BaSO₄ in fresh water = $2.33 \times 10^{-3} \text{ g L}^{-1}$

$$= \frac{2.33 \times 10^{-3}}{233} \text{ mol L}^{-1} = 10^{-5} \text{ M}$$

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (10^{-5})^2 = 10^{-10}$$

Now let x be the solubility in mol L⁻¹ in H₂SO₄

$$\Rightarrow [\text{Ba}^{2+}] \text{ in solution} = x \text{ mol L}^{-1}$$

$$\text{and } [\text{SO}_4^{2-}] \text{ in solution} = (x + 0.005) \text{ mol L}^{-1}$$

$$\text{Ionic product} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (x)(x + 0.005)$$

$$K_{sp} = \text{Ionic product at equilibrium (saturation)}$$

$$\Rightarrow 1.0 \times 10^{-10} = (x)(x + 0.005)$$

Assuming x to be a small number $(x + 0.005) \approx 0.005$

$$\Rightarrow x = \frac{10^{-10}}{0.005} = 2 \times 10^{-8} \text{ mol L}^{-1}$$

$$= 2 \times 10^{-8} \times 233 \text{ g L}^{-1}$$

$$= 4.66 \times 10^{-6} \text{ g L}^{-1}$$

$$\Rightarrow 4.66 \times 10^{-6} \text{ g of BaSO}_4 \text{ is washed away.}$$

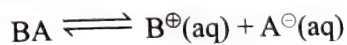
$$\Rightarrow \% \text{ loss} = \frac{4.66 \times 10^{-6} \times 100}{0.2} = 2.33 \times 10^{-3} \%$$

9 APPLICATION OF K_{sp} (PRECIPITATION OF SALTS)

a. **Purification of NaCl:** Sea water contains NaCl, Na_2SO_4 and MgSO_4 alongwith other impurities. On passing HCl gas through a saturated solution of NaCl, then NaCl is precipitated due to increased concentration (activity) of Cl^- ion available from the dissociation of HCl. NaCl thus obtained is of high purity and free from impurities. Similarly, soap (which is sodium salt of higher fatty acids) is precipitated out from its solution by stirring with NaCl. The process is called 'Salting out'.

b. **Predicting ionic or precipitation reaction:** To determine whether or not a precipitate will form when two solutions of known concentrations are mixed together. Consider the expression of the solubility product.

For a salt (sparingly soluble) when dissolved in water:



At equilibrium (saturation): $K_{sp} = [\text{B}^+][\text{A}^-]$

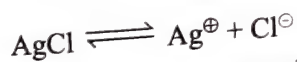
When we mix ions or if there be two or more ions in water, we define reaction coefficient (Q) called as ionic product, (I.P) giving the products of ions in water (ions of soluble salts and other common ions).

Ionic product is product of ionic concentration due to ions already present in water or from a salt. It may be and may not be equal to K_{sp} .

To illustrate it more clearly, consider a case when 500 mL of 0.005 M solution of AgNO_3 is added to 500 mL of 0.001 M solution of KCl. Now in solution (mixture), there are Ag^+ , NO_3^- , K^+ , and Cl^- ions. The concentration of $[\text{Ag}^+] = [\text{NO}_3^-] = 0.005/2 = 0.0025 \text{ M}$ (equal volumes are mixed)

and $[\text{K}^+] = [\text{Cl}^-] = \frac{0.001}{2} = 0.0005 \text{ M}$ as equal volumes of two solutions are mixed.

Now, we know that Ag^+ will react with Cl^- ions to form AgCl since:



is a reversible reaction with a high tendency towards left (solidifying or precipitating).

Now, question is, whether AgCl will be formed or not (precipitation of Ag^+ and Cl^- as AgCl) and if it is formed, how much of it will be formed? For this, we define some rules:

- If Ionic product $> K_{sp}$, precipitation takes place till ionic product equals K_{sp} .
- If ionic product $< K_{sp}$, a precipitate will not be formed and the solution will be unsaturated.
- If ionic product $= K_{sp}$, a precipitate just begins to form and the solution is saturated in that salt.
(or we can say that the solution is at a critical stage, when precipitation just begins, but actually has not occurred)

$$\begin{aligned}\text{In present case, ionic product} &= [\text{Ag}^+][\text{Cl}^-] \\ &= (0.0025)(0.0005) \\ &= 1.25 \times 10^{-7}\end{aligned}$$

(Only for the salt which is sparingly soluble, not for KNO_3)
Ionic product $> K_{sp}$ in this case ($K_{sp} \text{AgCl} = 1.56 \times 10^{-10}$) which means precipitation takes place.

ILLUSTRATION 8.111

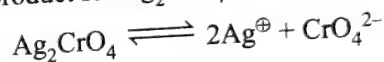
When 15 mL of 0.05 M AgNO_3 is mixed with 45.0 mL of 0.03 M K_2CrO_4 , predict whether precipitation of Ag_2CrO_4 occurs or not? (K_{sp} of $\text{Ag}_2\text{CrO}_4 = 1.9 \times 10^{-12}$)

Sol. First find the concentrations of Ag^+ and CrO_4^{2-} ions in the resulting mixture.

$$[\text{Ag}^+] = \frac{15 \times 0.05}{15 + 45} = 1.25 \times 10^{-2} \text{ M}$$

$$[\text{CrO}_4^{2-}] = \frac{45 \times 0.03}{15 + 45} = 2.25 \times 10^{-2} \text{ M}$$

The ionic product for Ag_2CrO_4 is given as follows:



$$\begin{aligned}\text{Ionic product} &= [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \\ &= (1.25 \times 10^{-2})^2(2.25 \times 10^{-2}) \\ &= 3.51 \times 10^{-6} > K_{sp}\end{aligned}$$

Hence, precipitation occurs.

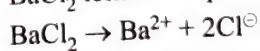
ILLUSTRATION 8.112

Given that solubility product of BaSO_4 is 1×10^{-10} . Will a precipitate be formed when

- Equal volumes of $2 \times 10^{-3} \text{ M}$ BaCl_2 solution and $2 \times 10^{-4} \text{ M}$ Na_2SO_4 solution, are mixed?
- Equal volumes of $2 \times 10^{-8} \text{ M}$ BaCl_2 solution and $2 \times 10^{-3} \text{ M}$ Na_2SO_4 solution, are mixed?
- 100 mL of 10^{-3} M BaCl_2 and 400 mL of 10^{-6} M Na_2SO_4 are mixed.

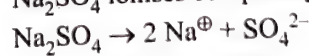
Sol.

- BaCl_2 ionises completely in the solution as



$$[\text{Ba}^{2+}] = [\text{BaCl}_2] = 2 \times 10^{-3} \text{ M (given)}$$

Na_2SO_4 ionises completely in the solution as



$$\therefore [\text{SO}_4^{2-}] = [\text{Na}_2\text{SO}_4] = 2 \times 10^{-4} \text{ M (given)}$$

Since equal volume of the two solutions are mixed together, the concentration of Ba^{2+} ions and SO_4^{2-} ions after mixing will be

$$[\text{Ba}^{2+}] = \frac{2 \times 10^{-3}}{2} = 10^{-3} \text{ M}$$

$$\text{and } [\text{SO}_4^{2-}] = \frac{2 \times 10^{-4}}{2} = 10^{-4} \text{ M}$$

$$\therefore \text{Ionic product of BaSO}_4 = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-3} \times 10^{-4} = 10^{-7}$$

which is greater than the solubility product (1×10^{-10}) of BaSO_4 . **Hence, a precipitate of BaSO_4 will be formed.**

b. Here, the concentration before mixing is:

$$[\text{Ba}^{2+}] = [\text{BaCl}_2] = 2 \times 10^{-8} \text{ M}$$

$$[\text{SO}_4^{2-}] = [\text{Na}_2\text{SO}_4] = 2 \times 10^{-3} \text{ M (Given)}$$

Concentration after mixing equal volumes will be

$$[\text{Ba}^{2+}] = \frac{2 \times 10^{-8}}{2} = 10^{-8} \text{ M}$$

$$[\text{SO}_4^{2-}] = \frac{2 \times 10^{-3}}{2} = 10^{-3} \text{ M}$$

$$\therefore \text{Ionic product of BaSO}_4 = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-8} \times 10^{-3} = 10^{-11}$$

which is less than the solubility product (1×10^{-10}).

Hence, no ppt will be formed in this case.

c. **Concentration of Ba^{2+}** (Total volume = $100 + 400 = 500 \text{ M}$)

$$M_1 V_1 = M_2 V_2$$

(Before) (After)

$$100 \times 10^{-3} = M_2 \times 500$$

$$M_2 = \frac{100 \times 10^{-3}}{500} = \frac{10^{-3}}{5} \text{ M}$$

Concentration of SO_4^{2-}

$$M_1 V_1 = M_2 V_2$$

(Before) (After)

$$400 \times 10^{-6} = M_2 \times 500$$

$$M_2 = \frac{400 \times 10^{-6}}{500} = \frac{4}{5} \times 10^{-6} \text{ M}$$

$$\text{IP (or) } Q_{\text{sp}} \text{ of BaSO}_4 = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$= \frac{10^{-3}}{5} \times \frac{4}{5} \times 10^{-6}$$

$$= \frac{4}{25} \times 10^{-9} \text{ M}^2$$

$$= 0.16 \times 10^{-9} \text{ M}^2 = 1.6 \times 10^{-10} \text{ M}^2$$

$$Q_{\text{sp}} > K_{\text{sp}}$$

So precipitate of BaSO_4 will occur.

ILLUSTRATION 8.113

The concentration of Ni^{2+} ions in a given NiS solution is $2.0 \times 10^{-6} \text{ M}$. Find the minimum S^{2-} ions necessary to cause precipitation of NiS . K_{sp} of $\text{NiS} = 1.4 \times 10^{-14}$.

Sol.

Note: Solubility product K_{sp} gives an idea of maximum possible concentration of an ion which can be retained in solution.

K_{sp} = ionic product for saturated solution



$$\text{Now, } K_{\text{sp}} = [\text{Ni}^{2+}][\text{S}^{2-}] \Rightarrow [\text{S}^{2-}] = \frac{K_{\text{sp}}}{[\text{Ni}^{2+}]}$$

It is the maximum permissible concentration of S^{2-} ion in solution.

For $[\text{S}^{2-}] = \frac{K_{\text{sp}}}{[\text{Ni}^{2+}]}$, NiS will just start to precipitate

If $[\text{S}^{2-}] > \frac{K_{\text{sp}}}{[\text{Ni}^{2+}]}$, NiS will precipitate.

This means $\frac{K_{\text{sp}}}{[\text{Ni}^{2+}]}$ is minimum concentration of S^{2-} ion above which precipitation occurs.

$$\Rightarrow [\text{S}^{2-}]_{\text{min}} = \frac{1.4 \times 10^{-14}}{2 \times 10^{-6}} = 7 \times 10^{-9} \text{ M}$$

8.20 APPLICATION OF k_{sp} IN QUALITATIVE SALT ANALYSIS

The separation and identification of various basic radicals into different group is mainly based upon six groups based on the increasing K_{sp} values of corresponding precipitating compounds.

Table 8.12 Analytical groups and their reagents

Grp.	Group reagent	Cations	Cations precipitated as
I.	Dilute HCl (2 M) in cold.	Hg_2^{2+} , Ag^+ , Pb^{2+}	Hg_2Cl_2 , AgCl , PbCl_2 (PbCl_2 is soluble in hot water, less in cold water).
II.	H_2S in presence of 0.2 M HCl	II A: Hg^{2+} , Pb^{2+} , Bi^{3+} , Cu^{2+} , Cd^{2+} II B: As^{3+} , As^{5+} , $\text{Sb}^{3+/+5}$, $\text{Sn}^{2+/+4}$	HgS , PbS , Bi_2S_3 , CuS , CdS , As_2S_3 , As_2S_5 , Sb_2S_3 , Sb_2S_5 , SnS , SnS_2
III.	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$	Fe^{3+} , Cr^{3+} , Al^{3+}	$\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$
IV.	H_2S in basic medium, i.e. $\text{H}_2\text{S} + \text{NH}_4\text{OH}$	Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+}	CoS , NiS , MnS , ZnS
V.	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$	Ba^{2+} , Sr^{2+} , Ca^{2+}	BaCO_3 , SrCO_3 , CaCO_3
VI.	No specific reagent	Na^+ , K^+ , Mg^{2+}	—
zero	Nessler's reagent in ammoniacal solution $\text{K}_2[\text{HgI}_4]$ + NH_4OH	NH_4^+	Iodide of Millon's base (Oxydimeric ammonium iodide) $\text{O} \begin{array}{c} \text{Hg} \\ \text{Hg} \end{array} \text{NH}_2\text{I}$

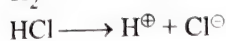
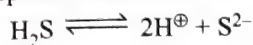
Increasing K_{sp} values

Group I: Dilute HCl is added to the solution containing cations. Since the K_{sp} values of the chlorides of group I is less than K_{sp} values of the chlorides of higher group, so only the chlorides of I groups are precipitated.

If the concentrated HCl is used, then $[\text{Cl}^-]$ will increase, then the ionic product (Q_{sp}) of their chlorides will increase, then chlorides of other group may be precipitated. Moreover, PbCl_2 is soluble in concentration HCl.

Group II: $\text{H}_2\text{S}(\text{g})$ is passed in an acidic medium to the solution containing cations. Since the K_{sp} values of the sulphides of group II ($\approx 10^{-28} - 10^{-54}$) is less than K_{sp} values of the sulphides of higher gr. ($> 10^{-28}$), so only the sulphides of group II are precipitated.

H_2S is a weak acid and its dissociation can be suppressed to get low $[\text{S}^{2-}]$ such that ionic products of group II sulphides are exceeded but not those of group III sulphides. This condition is achieved by passing H_2S in an acid medium so that H^+ (the common ion) suppress the dissociation of H_2S .

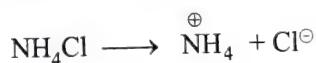
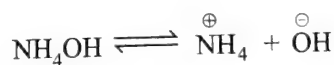


Thus, the group II sulphides are precipitated but not of other groups under these conditions because their K_{sp} values are quite high.

Note: Pb^{2+} is included in both groups I and II. PbCl_2 is sparingly soluble in dil HCl. Any Pb^{2+} ion present in group I filtrate will get precipitated as PbS in group II.

Group III: Hydroxides of group III are precipitated by adding an excess of solid NH_4Cl to the solutions of these cations followed by the addition of excess of NH_4OH .

NH_4OH is a weak base and is slightly ionised, whereas NH_4Cl being a strong electrolyte, ionises almost completely to give large $[\text{NH}_4^+]$ ions.



Due to common ion effect, the suppression of ionisation of NH_4OH occurs and $[\text{OH}^-]$ decreases appreciably. But even with this low $[\text{OH}^-]$ ions, exceed the low value of the K_{sp} of their hydroxides. Hence, only the hydroxides of group III get precipitated but not of other groups under these conditions because the K_{sp} of their hydroxides are quite high.

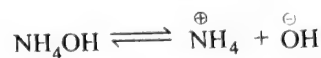
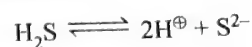
Note:

- NaOH cannot be used in place of NH_4OH , being a strong base, $[\text{OH}^-]$ will be high, and hence the hydroxides of the other group will precipitate out.
- NH_4OH should be added only after adding NH_4Cl , otherwise common ion effect would not occur in absence of NH_4Cl . Hence, hydroxides of other group will be precipitated out.
- NaCl and NaOH cannot be used in place of NH_4Cl and NH_4OH . Both being strong ionises completely to give high $[\text{OH}^-]$. NaCl cannot suppress the ionisation of NaOH . Therefore, hydroxides of other group will precipitate out. Moreover, $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ are soluble in excess of NaOH because of the formation of aluminate and chromate, respectively.

Group IV: Precipitation of sulphides of group IV occurs in presence of large excess of NH_4OH . K_{sp} of sulphides of group IV

are sufficiently high. Therefore high concentration of S^{2-} ions as compared to that required in group II for which K_{sp} values are low.

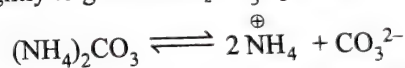
H_2S is weakly ionised as:



In presence of NH_4OH , OH^- ions neutralise H^+ ions. According to Le Chatelier's principle, ionization of H_2S proceeds in forward direction. Therefore, $[\text{S}^{2-}]$ increases. Ultimately, the ionic products of the sulphides of group IV exceeds the K_{sp} of their corresponding metal sulphides and hence get precipitated.

Note: $(\text{NH}_4)_2\text{SO}_4$ can not be used in place of NH_4OH , because the sulphates of Ba, Ca and Sr. will get precipitated as white precipitate.

Group V: The carbonates of group V are precipitated by adding $(\text{NH}_4)_2\text{CO}_3$ solution to the solution of these cations in the presence of NH_4Cl and NH_4OH . $(\text{NH}_4)_2\text{CO}_3$ is a weak electrolyte that ionises slightly to give small $[\text{CO}_3^{2-}]$ ions.



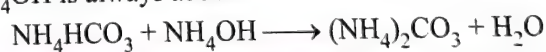
NH_4Cl is a strong electrolyte, ionises almost completely to

give large $[\text{NH}_4^+]$. Due to the common ion effect, the dissociation of $(\text{NH}_4)_2\text{CO}_3$ is suppressed and hence high $[\text{CO}_3^{2-}]$ decreases considerably. But even with this low $[\text{CO}_3^{2-}]$ ions, the ionic products of these cations and CO_3^{2-} ions exceed the low K_{sp} values of their corresponding metal carbonates and thus get precipitated.

Note: However, under these conditions, Mg salts do not get precipitated as MgCO_3 since its K_{sp} value is comparatively high and thus requires a high $[\text{CO}_3^{2-}]$ ions for precipitation.

The carbonates of Na^+ , K^+ , and NH_4^+ are also not precipitated because they are quite soluble.

The necessity of adding NH_4OH arises due to the fact that $(\text{NH}_4)_2\text{CO}_3$ solution usually contains a large amount of NH_4HCO_3 . Thus, the cations of group V will form not only insoluble carbonates but also soluble bicarbonates. As a result, the precipitation will not be complete. In order to convert NH_4HCO_3 , NH_4OH is always added.



Note:

- Na_2CO_3 cannot be used in place of $(\text{NH}_4)_2\text{CO}_3$ because Na_2CO_3 is a strong electrolyte whose ionisation cannot be suppressed by common ion effect. Therefore, the large $[\text{CO}_3^{2-}]$ ions will also precipitate magnesium.
- Large excess of NH_4Cl should be avoided. Since the large excess of NH_4Cl further reduces the $[\text{CO}_3^{2-}]$ ions, to such a low value that it even does not exceed the K_{sp} of group V radicals.
- The solution should be warmed and not boiled while precipitating group V radicals. Since warming decomposes the soluble bicarbonates (impurities) of Ca, Sr and Ba into insoluble carbonates.



Boiling dissolves the insoluble carbonates as chlorides.



- d. The group V precipitates should be dissolved in acetic acid. If the precipitates are dissolved in strong acid like HCl or HNO_3 , Ca will not get precipitated as calcium oxalate by adding ammonium oxalate because it is soluble in strong acid.

H_2SO_4 precipitates sulphates of Ca, Ba, and Sr.

ILLUSTRATION 8.114

A solution contains 0.01 M each of CaCl_2 and SrCl_2 . A 0.005 M solution of SO_4^{2-} is slowly added to the given solution.

- Which substance begins to precipitate first?
 - If H_2SO_4 is continuously added, determine when will other salt be precipitated?
 - When second salt starts to precipitate, find the concentration of cation of first salt.
- Assume that CaCl_2 and SrCl_2 are 100% ionised and volume of the solution remains constant.
 $(K_{\text{sp}} \text{ of } \text{SrSO}_4 = 3.2 \times 10^{-7} \text{ and } K_{\text{sp}} \text{ of } \text{CaSO}_4 = 1.3 \times 10^{-4})$

Sol. The solution 0.01 M Ca^{2+} ion and 0.01 M Sr^{2+} ions (100% ionisation). Now SO_4^{2-} ions are added gradually and slowly.

- First calculate the minimum $[\text{SO}_4^{2-}]$ required to start precipitation of CaSO_4 and SrSO_4 .

$$[\text{SO}_4^{2-}]_{\text{Min. for CaSO}_4} = \frac{K_{\text{sp}}[\text{CaSO}_4]}{[\text{Ca}^{2+}]} \\ = \frac{1.3 \times 10^{-4}}{0.01} = 1.3 \times 10^{-5} \text{ M}$$

$$\text{Since } [\text{SO}_4^{2-}]_{\text{Min. for SrSO}_4} = \frac{K_{\text{sp}}[\text{SrSO}_4]}{[\text{Sr}^{2+}]} \\ = \frac{3.2 \times 10^{-7}}{0.01} = 3.2 \times 10^{-5} \text{ M}$$

Since $[\text{SO}_4^{2-}]$ for SrSO_4 is much lower that required for CaSO_4 , so SrSO_4 will precipitate first.

- Now, if SO_4^{2-} ions are continuously added, at some instant, its concentration will become equal to that minimum required for precipitating out Ca^{2+} ions.

Hence CaSO_4 will start precipitating if,

$$[\text{SO}_4^{2-}] = 1.3 \times 10^{-5} \text{ M}.$$

- Now, find the concentration of Sr^{2+} ions when $[\text{SO}_4^{2-}] = 1.3 \times 10^{-5} \text{ M}$ in the solution.

$$[\text{Sr}^{2+}] = \frac{K_{\text{sp}}\text{SrSO}_4}{[\text{SO}_4^{2-}]} = \frac{3.2 \times 10^{-7}}{1.3 \times 10^{-5}} = 2.46 \times 10^{-5} \text{ M}$$

$$[2.46 \times 10^{-5} \text{ M} \lll 0.01 \text{ M}]$$

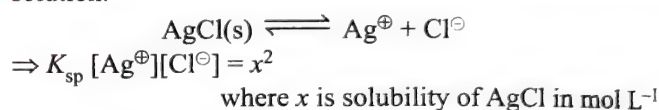
Note that when CaSO_4 starts to precipitate, SrSO_4 is almost precipitated out as the value of Sr^{2+} is very very low.

Note: The above illustration represents a case of selective precipitation (or separation of metals cations) by adding a common anion. Note that there is a vast difference in the K_{sp} value of two sulphates, and hence in the minimum values of sulphate ion for precipitating out the two metals ions.

ILLUSTRATION 8.115

How much the concentration of Ag^{\oplus} ions in a saturated solution of AgCl diminish if such an amount of HCl is added to it that the concentration of Cl^{\ominus} ions in the solution becomes equal to 0.03 M? Also find the amount of AgCl precipitated at the given concentration. K_{sp} of $\text{AgCl} = 1.8 \times 10^{-10}$.

Sol. HCl is added to a solution containing Ag^{\oplus} ions in saturated solution. First find the concentration of Ag^{\oplus} ion in this solution.



where x is solubility of AgCl in mol L^{-1}

$$\Rightarrow [\text{Ag}^{\oplus}] = \sqrt{K_{\text{sp}}} = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} \text{ M}$$

When HCl is added, the ionic product of AgCl approaches the K_{sp} value of AgCl , the precipitation of Ag^{\oplus} ions will occur. As ionic product increases (i.e., becomes greater than K_{sp} value), and appreciable amount of AgCl precipitates out, and precipitation continues till ionic product equals solubility product (K_{sp}).

$$\text{Ionic product} = [\text{Ag}^{\oplus}][\text{Cl}^{\ominus}] = K_{\text{sp}}$$

$$\Rightarrow [\text{Ag}^{\oplus}] = \frac{K_{\text{sp}}}{[\text{Cl}^{\ominus}]} = \frac{1.8 \times 10^{-10}}{(0.03)} = 6.0 \times 10^{-9} \text{ M}$$

Now this is the amount of Ag^{\oplus} ions left un-precipitated.

$\Rightarrow [\text{Ag}^{\oplus}]$ diminishes in the solution by

$$\frac{6.0 \times 10^{-9}}{1.34 \times 10^{-5}} = \left(\frac{1}{2233} \right) \text{ times}$$

The concentration of AgCl precipitated out of the solution

$$= [\text{Ag}^{\oplus}]_{\text{initial}} - [\text{Ag}^{\oplus}]_{\text{left}} \\ = 1.34 \times 10^{-5} - 6.0 \times 10^{-9} \text{ M}$$

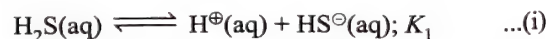
It means almost whole of AgCl is precipitated out of the solution at $[\text{Cl}^{\ominus}] = 0.03 \text{ M}$.

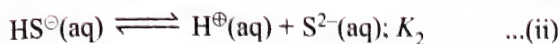
8.21 PRECIPITATION THROUGH H_2S

The most typical technique used in precipitating the metals ions or selectively precipitating (separation) the two metal ions, is passing H_2S gas in a solution of metal ion (s) whose acidity is externally controlled (or preset by adding HCl). First consider the ionisation (equilibrium) of H_2S gas in an aqueous solution and then in an acidic solution.

8.21.1 PASSING $\text{H}_2\text{S(g)}$ IN AN AQUEOUS SOLUTION

H_2S is a dibasic acid. We have to visualise two-stage ionisation for it





K_1 and K_2 are first and second ionisation constants, respectively, for $\text{H}_2\text{S}(\text{aq})$. Since $K_2 \ll K_1$ (due to common ion effect), we usually neglect the concentration of H^{\oplus} ions from second equilibrium.

$$\Rightarrow [\text{H}^{\oplus}]_{\text{in solution}} = [\text{H}^{\oplus}]_{\text{from } \text{H}_2\text{S}} + [\text{H}^{\oplus}]_{\text{from } \text{HS}^{\ominus}} \\ \approx [\text{H}^{\oplus}]_{\text{from } \text{H}_2\text{S}}$$

$$\text{Now, } K_1 = \frac{[\text{H}^{\oplus}][\text{HS}^{\ominus}]}{[\text{H}_2\text{S}]} \text{ and } K_2 = \frac{[\text{H}^{\oplus}][\text{S}^{2-}]}{[\text{HS}^{\ominus}]}$$

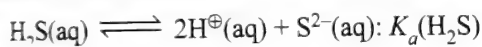
From equation (i), $[\text{H}^{\oplus}] = [\text{HS}^{\ominus}]$ and neglecting $[\text{H}^{\oplus}]$ from equation (ii), we have from second ionisation constant:

$$K_2 = \frac{[\text{H}^{\oplus}][\text{S}^{2-}]}{[\text{HS}^{\ominus}]} \approx [\text{S}^{2-}] \text{ or } [\text{S}^{2-}] \approx K_2$$

So if we pass H_2S in an aqueous solution, sulphide ion concentration is simply equal to the value of second ionisation constant. We can determine whether precipitation of metal sulphide will occur or not by comparing ionic product with solubility constant (K_{sp}).

8.21.2 PASSING $\text{H}_2\text{S}(\text{g})$ IN AN ACIDIC SOLUTION

Now if we pass H_2S in an acidic solution of a metal ion till saturation, we simply neglect the concentration of H^{\oplus} ion from H_2S (both from first and second ionisation) totally as the concentration of H^{\oplus} from acid (strong acid added externally) is very high. In that case we can simply add two equilibria (i) and (ii) to get:



$$K_a = K_1 \times K_2 = \frac{[\text{H}^{\oplus}]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

Note that in saturated solution of H_2S at 25°C , $[\text{H}_2\text{S}]$ is constant at 0.1 M.

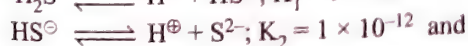
$$\Rightarrow K_a \times (0.1 \text{ M}) = [\text{H}^{\oplus}]^2[\text{S}^{2-}] \\ ([\text{H}^{\oplus}]^2[\text{S}^{2-}] = K_{\text{sp}} \text{ of } \text{H}_2\text{S})$$

$$\Rightarrow [\text{S}^{2-}] = \frac{K_a \times (0.1 \text{ M})}{[\text{H}^{\oplus}]^2} = \frac{K_1 \times K_2 \times (0.1 \text{ M})}{[\text{H}^{\oplus}]^2}$$

In this way, we now know the concentration of sulphide ion in an acidic solution, so accordingly we can plan precipitation of metal ions. The important aspect of this method is that we can always increase or decrease the concentration of sulphide ion by controlling the amount of acid.

ILLUSTRATION 8.116

Calculate the maximum possible concentration of Mn^{2+} in water that is saturated with H_2S (which is 0.1 M at 300 K) and maintained at pH = 3 with HCl. The equilibrium constant (s) for dissociation of H_2S are:



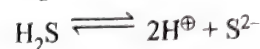
$$K_{\text{sp}} \text{ of } \text{MnS} = 3 \times 10^{-22}$$

Sol. Note that solution contains S^{2-} ions (from H_2S).

So Mn^{2+} will react with S^{2-} ions to give a precipitate of MnS (being sparingly soluble salt). Hence, the concentration of S^{2-} at saturation will determine the maximum possible concentration of S^{2-} at saturation will determine the maximum possible concentration of Mn^{2+} ions in solution that will not be precipitating. So first calculate $[\text{S}^{2-}]$ at saturation.

Calculate K_a for dissociation of H_2S .

$$K_a \text{ of } \text{H}_2\text{S} = K_1 \times K_2 = 9 \times 10^{-20}$$



$$\Rightarrow K_a = \frac{[\text{H}^{\oplus}]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \Rightarrow [\text{S}^{2-}] = \frac{K_a[\text{H}_2\text{S}]}{[\text{H}^{\oplus}]^2}$$

Note that pH of solution is maintained at 3 (externally).

$$\Rightarrow [\text{H}^{\oplus}] = 10^{-3} \text{ M}$$

$$\Rightarrow [\text{S}^{2-}] = \frac{9 \times 10^{-20} \times 0.1}{(10^{-3})^2} = 9 \times 10^{-15}$$

In a saturated solution, ionic product = K_{sp}

$$\text{Now ionic product} = [\text{Mn}^{2+}][\text{S}^{2-}] = [\text{Mn}^{2+}](9 \times 10^{-15})$$

$$\Rightarrow [\text{Mn}^{2+}](9 \times 10^{-15}) = 3 \times 10^{-22}$$

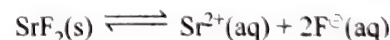
$$\Rightarrow [\text{Mn}^{2+}] = 3.33 \times 10^{-8} \text{ M}$$

8.22 SIMULTANEOUS EQUILIBRIUM

When two salts having a common ion (either cation or anion) are together in water, then their respective solubilities are not independent of each other.

Explanation of the concept: Consider a solution containing two salts: CaF_2 ($K_{\text{sp}} = 3.4 \times 10^{-11}$) and SrF_2 ($K_{\text{sp}} = 2.9 \times 10^{-9}$). Compare their K_{sp} values. Let us assume that most of F^{\ominus} ion concentration in the saturated solution is from SrF_2 , as its K_{sp} is much higher than that of CaF_2 . It means that first SrF_2 will establish its equilibrium (as if there is no CaF_2), then CaF_2 will dissolve in presence of ions furnished only by SrF_2 .

Let the solubility of SrF_2 be $x \text{ mol L}^{-1}$.



$$\Rightarrow [\text{Sr}^{2+}] = x \text{ and } [\text{F}^{\ominus}] = 2x$$

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^{\ominus}]^2 = (x)(2x)^2 = 4x^3$$

$$\Rightarrow x = \left(\frac{K_{\text{sp}}}{4} \right)^{1/3} = \left(\frac{2.9 \times 10^{-9}}{4} \right)^{1/3} = 9 \times 10^{-4}$$

Now the solubility of CaF_2 is determined in presence of $9 \times 10^{-4} \text{ M F}^{\ominus}$ ions. It means neglect the contribution of F^{\ominus} ions from CaF_2 .

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^{\ominus}]^2$$

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}}}{[\text{F}^{\ominus}]^2} = \frac{3.4 \times 10^{-11}}{(2 \times 9 \times 10^{-4})^2} = 1.0 \times 10^{-5} \text{ M}$$

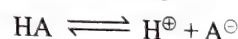
Hence, the solubility of CaF_2 is $1.0 \times 10^{-5} \text{ mol L}^{-1}$.

Note: Let us check our assumption. F^\ominus ions from CaF_2 is twice the amount of Ca^{2+} ions i.e., 2.0×10^{-5} M, whereas F^\ominus ions from SrF_2 is $2 \times 9.0 \times 10^{-4}$, i.e. 1.8×10^{-3} M, which is much higher than 2.0×10^{-5} M.

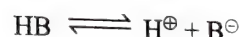
ILLUSTRATION 8.117

Two weak monobasic organic acids HA and HB have dissociation constants as 3.0×10^{-5} and 1.5×10^{-5} , respectively, at $25^\circ C$. If 500 mL of 1 M solutions of each of these two acids are mixed to produce 1 L of mixed acid solution, what is the pH of the resulting solution?

Sol. Note that K_a of two acids is nearly same. In such cases, we have to consider H^\oplus from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 0.5 M [equal volumes are mixed] = C M



C



C



Now, $[H^\oplus]_{\text{final}} = [H^\oplus]_{\text{from HA}} + [H^\oplus]_{\text{from HB}}$

$$\Rightarrow K_{a(\text{HA})} = \frac{(x+y)x}{C-x} \text{ and } K_{a(\text{HB})} = \frac{(x+y)y}{C-y}$$

As K_a of both acid $\approx 10^{-5}$ and H^\oplus from one acid acts as common ion for other's dissociation, x and y are very less as compared to C .

$$\Rightarrow C - x \approx C \text{ and } C - y \approx C$$

$$\Rightarrow K_{a(\text{HA})} = \frac{(x+y)x}{C} \text{ and } K_{a(\text{HB})} = \frac{(x+y)y}{C}$$

Divide the two expressions to get:

$$\frac{1}{2} = \frac{x}{y} \Rightarrow x = 2y$$

$$\text{Substitute for } y = \frac{1}{2}x \text{ in } K_{a(\text{HA})} = \frac{x^2 + xy}{C}$$

$$\Rightarrow 3.0 \times 10^{-5} = \frac{x^2 + 0.5x^2}{0.5}$$

$$\Rightarrow x = \sqrt{10} \times 10^{-3} \text{ M and } y = \frac{\sqrt{10}}{2} \times 10^{-3} \text{ M}$$

$$[H^\oplus] = x + y = \frac{3\sqrt{10}}{2} \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log \left(\frac{3\sqrt{10}}{2} \times 10^{-3} \right) \Rightarrow \text{pH} = 2.32$$

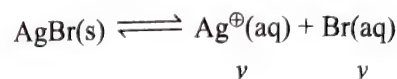
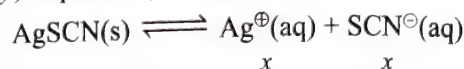
ILLUSTRATION 8.118

Calculate the simultaneous solubilities of AgSCN and AgBr.

$$[K_{sp}(\text{AgSCN}) = 1.0 \times 10^{-12}; K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}]$$

Sol. In this case, please note that the K_{sp} values of two salts are very similar. So the concentration of Ag^\oplus ions (the common ion) cannot be calculated from a single salt alone and we have to consider the equilibrium of the two salts simultaneously.

Let the simultaneous solubilities of AgSCN and AgBr be x and y , respectively, in mol L^{-1} .



At equilibrium:

$$[Ag^\oplus] = x + y; [SCN^\ominus] = x; [Br^\ominus] = y$$

$$[Ag^\oplus][Br^\ominus] = K_{sp}(\text{AgBr})$$

$$\text{and } [Ag^\oplus][SCN^\ominus] = K_{sp}(\text{AgSCN})$$

According to electrical charge neutrality equation.

Total positive charge = Total negative charge

$$\text{Note that: } [Ag^\oplus] = [Br^\ominus] + [SCN^\ominus]$$

[This is an Electrical charge neutrality equation]

$$[Ag^\oplus] = \frac{K_{sp}(\text{AgBr})}{[Br^\ominus]} + \frac{K_{sp}(\text{AgSCN})}{[Ag^\oplus]}$$

$$\Rightarrow [Ag^\oplus] = \sqrt{K_{sp}(\text{AgBr}) + K_{sp}(\text{AgSCN})}$$

$$\Rightarrow x + y = 1.22 \times 10^{-6} \quad \dots(i)$$

$$\text{Also, } \frac{[Br^\ominus]}{[SCN^\ominus]} = \frac{y}{x} = \frac{K_{sp}(\text{AgBr})}{K_{sp}(\text{AgSCN})} = 0.5 \quad \dots(ii)$$

Using equations (i) and (ii), we get

$$x = 8.0 \times 10^{-7}; y = 4.0 \times 10^{-7}$$

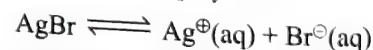
ILLUSTRATION 8.119

How much AgBr could dissolve in 1.0 L of 0.4 M NH_3 ? Assume that $Ag(NH_3)_2^\oplus$ is the only complex formed. Given: the dissociation constant for



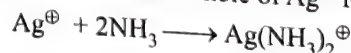
$$K_d = 6.0 \times 10^{-8} \text{ and } K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}.$$

Sol. Let solubility of AgBr be x M. Thus, $[Br^\ominus] = x$ M, but $[Ag^\oplus] \neq x$ M since it will react with NH_3 to form a complex and thus, its concentration will be decided by the dissociation of complex. So, let $[Ag^\oplus] = y$ M.



$$\Rightarrow K_{sp} = [Ag^\oplus][Br^\ominus] = yx = 5.0 \times 10^{-13}$$

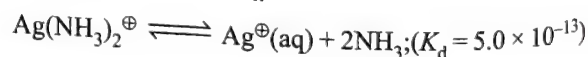
Since the formation constant (K_f) of the complex is very high, assume that whole of Ag^\oplus formed is consumed.



$x \quad 0.4$

$0.4 - 2x$

x



x

$0.4 - 2x$

$x - y$

$y \quad 0.4 - 2x + 2y$

$$\text{Thus, } K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{y(0.4 - 2x + 2y)^2}{x - y} = 6 \times 10^{-8}$$

Assuming $x - y \approx x$ since K_d is low and $x \ll 0.4$, we get

$$K_d = \frac{y(0.4)^2}{x}$$

Solving for x :

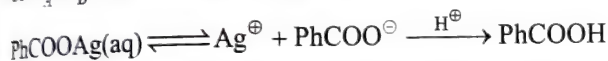
$$x = 1.15 \times 10^{-3} \text{ M}$$

(Verify the approximation yourself)

8.23 THE SOLUBILITY OF A SALT OF WEAK ACID IN PRESENCE OF H^+ IONS FROM BUFFER SOLUTION

The solubility of salts of weak acid increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increases the solubility of the salt, so that $K_{sp} = Q_{sp}$.

For example, the solubility of silver benzoate (PhCOOAg) (salt of W_A) in presence of H^+ ions.



According to Le Chatelier's principle, ionisation of salt increases and hence solubility increases.

Rule: Solubility of salt of W_A increases with increase in $[\text{H}^+]$ ions or increases at lower pH.

Formula of solubility of salt of W_A in presence of H^+ ions:

The two equilibrium must be satisfied simultaneously, Let the salt of W_A is represented as MX .

$$K_{sp} = [\text{M}^+][\text{X}^-] \quad \dots(i)$$

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

$$\frac{[\text{X}^-]}{[\text{HX}]} = \frac{K_a}{[\text{H}^+]} \quad \dots(ii)$$

Taking inverse of both sides and adding 1 to eq (ii) we get,

$$\frac{[\text{HX}]}{[\text{X}^-]} + 1 = \frac{[\text{H}^+]}{K_a} + 1$$

$$\frac{[\text{HX}] + [\text{X}^-]}{[\text{X}^-]} = \frac{[\text{H}^+] + K_a}{K_a} \quad \dots(iii)$$

Now, again taking inverse of equation (iii), we get

$$\frac{[\text{X}^-]}{[\text{HX}] + [\text{X}^-]} = \frac{K_a}{[\text{H}^+] + K_a}$$

At a particular value of $[\text{H}^+]$

$$\therefore \frac{[\text{X}^-]}{[\text{X}^-] + [\text{HX}]} = f = \frac{K_a}{K_a + [\text{H}^+]}$$

It can be seen as 'f' decreases as pH increases. If S_{new} is the solubility of the salt at given pH, then

$$K_{sp} = [S_{\text{new}}][fS_{\text{new}}] = S_{\text{new}}^2 \left[\frac{K_a}{K_a + [\text{H}^+]} \right]$$

$$\text{or } S_{\text{new}} = \left[\frac{K_{sp}[\text{H}^+] + K_a}{K_a} \right]^{1/2} = \left[K_{sp} \left(1 + \frac{[\text{H}^+]}{K_a} \right) \right]^{1/2}$$

Thus, solubility S increases with increase in $[\text{H}^+]$ or decrease in pH.

$$\therefore S_{\text{H}_2\text{O}} = \sqrt{K_{sp}} \quad (\because K_{sp} = S^2)$$

Ratio of solubilities of salt of W_A in presence of H^+ ions and in H_2O is:

$$\frac{S_{\text{new}}}{S_{\text{H}_2\text{O}}} = \frac{\sqrt{K_{sp}} \left[1 + \frac{[\text{H}^+]}{K_a} \right]^{1/2}}{\sqrt{K_{sp}}} = \left(1 + \frac{[\text{H}^+]}{K_a} \right)^{1/2}$$

ILLUSTRATION 8.120

The solubility of silver benzoate (PhCOOAg) in H_2O and in a buffer solution of pH = 4, 5, and 6 are S_1 , S_2 , S_3 , and S_4 , respectively. Give the decreasing order of their solubilities.

Sol. Solubility of a salt of W_A increases with the increase in $[\text{H}^+]$ or increases at lower pH. Thus, decreasing order of solubility is:

$$S_2 > S_3 > S_4 > S_1$$

ILLUSTRATION 8.121

The ionisation constant of benzoic acid (PhCOOH) is 6.45×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13} . How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

Sol. K_a of $\text{PhCOOAg} = 6.45 \times 10^{-5}$

$$K_{sp} \text{ of } \text{PhCOOAg} = 2.5 \times 10^{-13}$$

$$\text{pH of buffer} = 3.19$$

$$\therefore [\text{H}^+] = \text{Antilog}(-3.19) = \text{Antilog}(-3 - 0.19 + 1 - 1)$$

$$= \text{Antilog}(\bar{4}.81)$$

$$= 6.45 \times 10^{-4} \text{ M}$$

Let S_{buffer} (solubility of salt in a buffer)

$$= \sqrt{K_{sp}} \left[1 + \frac{[\text{H}^+]}{K_a} \right]^{1/2}$$

$$S_{\text{H}_2\text{O}} = \sqrt{K_{sp}}$$

$$\therefore \frac{S_{\text{buffer}}}{S_{\text{H}_2\text{O}}} = \frac{\sqrt{K_{sp}} \left[1 + \frac{[\text{H}^+]}{K_a} \right]^{1/2}}{\sqrt{K_{sp}}}$$

$$= \left[1 + \frac{6.45 \times 10^{-4}}{6.45 \times 10^{-5}} \right]^{1/2}$$

$$= [1 + 10]^{1/2} = (11)^{1/2} = 3.317$$

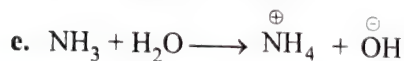
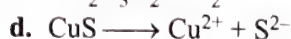
Thus, silver benzoate is 3.317 times more soluble at lower pH than in water.

ILLUSTRATION 8.122

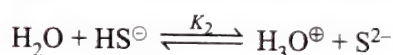
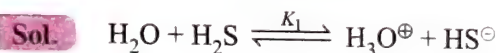
Write equations showing all of the equilibrium reactions occurring in aqueous solutions containing each of the following sets of reagents.

- NaCl
- NaOH
- $\text{NaC}_2\text{H}_3\text{O}_2 + \text{HC}_2\text{H}_3\text{O}_2$
- $\text{Na}_2\text{S} + \text{CuS}$
- $\text{NH}_4\text{Cl} + \text{NH}_3 + \text{Mg}(\text{OH})_2(\text{s})$

Sol. All of them (a)–(e) involve: $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$. In addition, (c) to (e) have following equilibrium:

**ILLUSTRATION 8.123**

Calculate the solubility of CoS in 0.1 M H_2S and 0.15 M H_3O^+ (K_{sp} of CoS = 3×10^{-26}). ($K_1 \times K_2(\text{H}_2\text{S}) = 10^{-21}$)



$$K_1 K_2 = \frac{[\text{H}_3\text{O}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = 10^{-21}$$

In 0.1 M H_2S and 0.15 M H_3O^+ ,

$$[\text{S}^{2-}] = \frac{(0.15)^2 [\text{S}^{2-}]}{0.1} = 10^{-21}$$

$$\therefore [\text{S}^{2-}] = \frac{10^{-22}}{0.0225} = 4 \times 10^{-21}$$

$$K_{\text{sp}} = [\text{Co}^{2+}][\text{S}^{2-}] = 3 \times 10^{-26}$$

$$[\text{Co}^{2+}] = \frac{3 \times 10^{-26}}{4 \times 10^{-21}} = 7 \times 10^{-6} \text{ M}$$

ILLUSTRATION 8.124

Explain why CoS is more soluble than predicted by the K_{sp} .

Sol. Not all the sulphide which dissolves remains as S^{2-} , most of it hydrolyses:

**ILLUSTRATION 8.125**

The solubility of CuS in pure water at 25°C is $3.3 \times 10^{-4} \text{ g L}^{-1}$. Calculate K_{sp} of CuS. The accurate value of K_{sp} of CuS was found to be 8.5×10^{-36} at 25°C .



$$S = \frac{3.3 \times 10^{-4} \text{ g L}^{-1}}{95.6 \text{ g mol}^{-1}} = 3.5 \times 10^{-6} \text{ M}$$

$$\text{Apparent } K_{\text{sp}} = (3.5 \times 10^{-6})^2 = 1.2 \times 10^{-11}$$

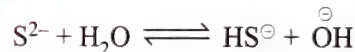
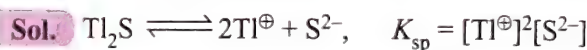
ILLUSTRATION 8.126

Explain why CuS is more soluble than predicted by the K_{sp} .

Sol. The S^{2-} hydrolyses extensively. The amount which dissolves and the amount which exists as S^{2-} in solution are very different.

ILLUSTRATION 8.127

The solubility of Ti_2S in pure CO_2 -free water is $6.3 \times 10^{-6} \text{ M}$. Assume that the dissolved S^{2-} ion hydrolyses almost completely to HS^- and that the further hydrolysis to H_2S is neglected. What is, K_{sp} ? ($K_2(\text{H}_2\text{S}) = 10^{-14}$)



$$K_h = \frac{K_w}{K_2} = \frac{10^{-14}}{10^{-14}} = 1.0$$

$$[\text{Ti}^+] = 2(6.3 \times 10^{-6}), \quad [\text{OH}^-] = [\text{HS}^-] = 6.3 \times 10^{-6}$$

$$K_h = \frac{(6.3 \times 10^{-6})^2}{[\text{S}^{2-}]} = 1.0, \therefore [\text{S}^{2-}] = (6.3 \times 10^{-6})^2$$

$$K_{\text{sp}} = (6.3 \times 10^{-6})^2 [2(6.3 \times 10^{-6})]^2 = 6.3 \times 10^{-21}$$

ILLUSTRATION 8.128

When solid SrCO_3 is equilibrated with a pH 8.60 buffer, the solution was found to have $[\text{Sr}^{2+}] = 2.2 \times 10^{-4}$. What is the K_{sp} of SrCO_3 ? (K_2 of $\text{H}_2\text{CO}_3 = 4.7 \times 10^{-11}$)

Sol. First Method (by using direct formula):

Solubility of salt of weak acid (H_2CO_3) in buffer (refer section 8.10.1) is given by the formula

$$S_{\text{buffer}} = \sqrt{K_{\text{sp}}} \left[1 + \frac{[\text{H}^+]}{K_a} \right]^{1/2} \quad \dots(i)$$

$$S_{\text{buffer}} = 2.2 \times 10^{-4} \text{ M, pH} = 8.60,$$

$$\therefore [\text{H}^+] = -\log(8.6) = 2.51 \times 10^{-9}$$

$$K_2 = 4.7 \times 10^{-11}$$

Substituting the value in equation (i), we get

$$2.2 \times 10^{-4} = (K_{\text{sp}})^{1/2} \left[1 + \frac{2.51 \times 10^{-9}}{4.7 \times 10^{-11}} \right]^{1/2}$$

$$= (K_{\text{sp}})^{1/2} (1 + 53.4)^{1/2}$$

$$\therefore K_{\text{sp}} = \frac{(2.2 \times 10^{-4})^2}{54.4} = 8.9 \times 10^{-10}$$

Second method:

$$K_{sp} = [Sr^{2+}][CO_3^{2-}]$$



$$K_h = \frac{K_w}{K_2} = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = \frac{K_w}{4.7 \times 10^{-11}}$$

$$[H_3O^+] = -(\log 8.6) = 2.51 \times 10^{-9}$$

$$[OH^-] = \frac{K_w}{2.51 \times 10^{-9}}$$

$$\left(\frac{K_w}{2.51 \times 10^{-9}} \right) \left[\frac{HCO_3^-}{CO_3^{2-}} \right] = \frac{K_w}{4.7 \times 10^{-11}}$$

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{2.51 \times 10^{-9}}{4.7 \times 10^{-11}} = 53.4$$

The CO_3^{2-} ion which dissolves forms HCO_3^- in a 1:1 mol ratio or remains unreacted, thus, by electroneutrality,

$$[Sr^{2+}] = [HCO_3^-] + [CO_3^{2-}]$$

$$2.2 \times 10^{-4} = 53.4[CO_3^{2-}] + [CO_3^{2-}]$$

$$2.2 \times 10^{-4} = 54.4[CO_3^{2-}]$$

$$\therefore [CO_3^{2-}] = \frac{2.2 \times 10^{-4}}{54.4}$$

$$K_{sp} = (2.2 \times 10^{-4}) \left(\frac{2.2 \times 10^{-4}}{54.4} \right) = 8.9 \times 10^{-10}$$

ILLUSTRATION 8.129

Calculate the solubility at 25°C of $CaCO_3$ in a closed container containing a solution of pH 8.60. [$K_{sp}(CaCO_3) = 10^{-8}$]

$$\text{Sol. } S_{\text{buffer}} = \sqrt{K_{sp} \left[1 + \frac{[H^+]}{K_a} \right]^{1/2}} \quad \dots(i)$$

$$= (10^{-8})^{1/2} \left[1 + \frac{2.51 \times 10^{-9}}{4.7 \times 10^{-11}} \right]^{1/2}$$

$$= (54.4 \times 10^{-8})^{1/2} = 7.376 \times 10^{-4} \approx 7.4 \times 10^{-4}$$

Second method (proceeding as in the last illustration)

By electroneutrality,

$$[Ca^{2+}] = [CO_3^{2-}] + [HCO_3^-]; \quad \frac{[HCO_3^-]}{[CO_3^{2-}]} = 53.4$$

$$\text{Let } x = [Ca^{2+}] = 54.4[CO_3^{2-}]$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

$$= x \left(\frac{x}{54.4} \right) = \frac{x^2}{54.4} = 10^{-8}$$

$$\therefore x = 7.4 \times 10^{-4} = [Ca^{2+}] = \text{Solubility}$$

CONCEPT APPLICATION EXERCISE 8.4**Objective Type****Indicators**

1. The pH range where the indicator shows change in colour are given as:

- i. 4–9.7 ii. 7.46–10.0 iii. 6.5–4

Which of the above pH range represents titration of

I. Strong acid/strong base (S_A/S_B),

II. Weak acid/strong base (W_A/S_B)

III. Weak base/strong acid (W_B/S_A)

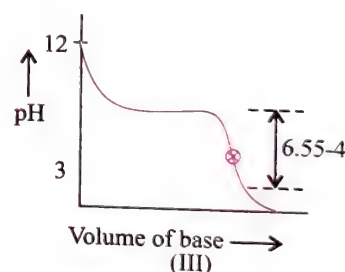
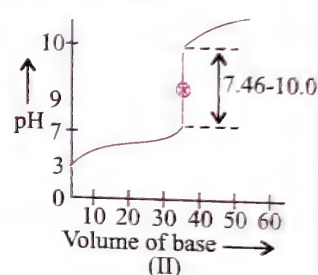
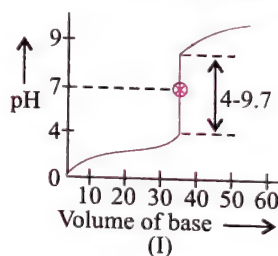
(1) (i) → I, (ii) → II, (iii) → III

(2) (iii) → I, (ii) → II, (i) → III

(3) (ii) → I, (iii) → II, (i) → III

(4) (i) → I, (iii) → II, (ii) → III

2. The acid base titration graphs are given as:



Which graph represents titration of

i. NH_4OH/HCl (W_B/S_A)

ii. HNO_3/KOH (S_A/S_B)

iii. C_6H_5COOH/KOH (W_A/S_B)

Graph**Titration**

(1) I, II, III

i, ii, iii

(2) I, II, III

ii, iii, i

(3) I, II, III

iii, ii, i

(4) I, II, III

iii, i, ii

3. Which indicator is suitable for the titrations:

Titration**Indicator**

i. $HCOOH/NaOH$

(A) Bromothymol blue or phenolphthalein or methyl orange or thymolphthalein.

ii. HBr/KOH

(B) Methyl orange or methyl red or bromocresol green

iii. NH_4OH/HNO_3

(C) Phenolphthalein or thymolphthalein

- (1) (i) \rightarrow A, (ii) \rightarrow B, (iii) \rightarrow C
 (2) (i) \rightarrow A, (ii) \rightarrow C, (iii) \rightarrow B
 (3) (i) \rightarrow B, (ii) \rightarrow C, (iii) \rightarrow A
 (4) (i) \rightarrow C, (ii) \rightarrow A, (iii) \rightarrow B

4. A solution gives the following colours with different indicators:

Methyl orange	Yellow
Methyl red	Yellow
Bromothymol blue	Orange

What is the pH of the solution?

- (1) >4.5 (2) >6.0
 (3) 6.0 to 6.3 (4) 4.5 to 6

5. In the titration of NH_4OH versus HCl , the pH of the solution at equivalence point is about:

- (1) 5.5 (2) 7
 (3) 8.5 (4) 9.5

6. The pH indicators are:

- (1) Salts of strong acids and strong bases
 (2) Salts of weak acids and weak bases
 (3) Either weak acids or weak bases
 (4) Either strong acids or strong bases

7. In which of the following acid-base titrations, pH is greater than 8 at the equivalence point?

- (1) Acetic acid vs ammonia
 (2) Acetic acid vs sodium hydroxide
 (3) Hydrochloric acid vs ammonia
 (4) Hydrochloric acid vs sodium hydroxide

8. Why are strong acids generally used as standard solutions in acid-base titrations?

- (1) The pH at the equivalent point will always be 7.
 (2) They can be used to titrate both strong and weak bases.
 (3) Strong acids form more stable solutions than weak acids.
 (4) The salts of strong acids do not hydrolyse.

9. The best indicator for detection of end point in titration of a weak acid and a strong base is

- (1) Methyl orange (3 to 4)
 (2) Methyl red (5 to 6)
 (3) Bromothymol blue (6 to 7.5)
 (4) Phenolphthalein (8 to 9.6)

Solubility and K_{sp}

10. The precipitate of CaF_2 is obtained when equal volumes of the following are mixed.

$$[K_{sp}(\text{CaF}_2) = 1.7 \times 10^{-10}]$$

- (1) $10^{-2} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^\ominus$
 (2) $10^{-4} \text{ M Ca}^{2+} + 10^{-4} \text{ M F}^\ominus$
 (3) $10^{-3} \text{ M Ca}^{2+} + 10^{-5} \text{ M F}^\ominus$
 (4) $10^{-5} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^\ominus$

11. The solubility of A_2B_3 is $x \text{ mol dm}^{-3}$. Its K_{sp} is

- (1) $6x^4$ (2) $64x^4$ (3) $36x^5$ (4) $108x^5$

12. The pH of Ca(OH)_2 is 10.6 at 25°C . K_{sp} of Ca(OH)_2 is

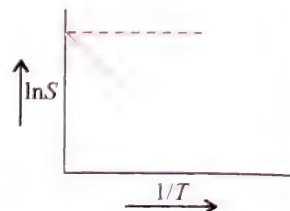
- (1) $3.2 \times 10^{-12} \text{ M}^3$ (2) $3.2 \times 10^{-11} \text{ M}^3$
 (3) $1.6 \times 10^{-12} \text{ M}^3$ (4) $1.6 \times 10^{-11} \text{ M}^3$

13. Solubility of AgI in 0.05 M BaI_2 solution is 10^{-15} M . The solubility of AgI in water is

- (1) 25×10^{-7} (2) 10^{-7} M (3) 5×10^{-8} (4) 10^{-8} M

14. The solubility (S) of a solute in water varies with temperature as given by $S = Ae^{-\Delta H/RT}$, ΔH being the enthalpy of solution.

For a given solute, variation of $\ln S$ with temperature is as shown in figure. The solute is expected to be



- (1) CaO (2) MgSO_4
 (3) CuSO_4 (4) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

15. The solubility of CaF_2 in a solution of $0.1 \text{ M Ca(NO}_3)_2$ is

- (1) $[\text{Ca}^{2+}]$ (2) $2[\text{F}^\ominus]$ (3) $\frac{[\text{F}^\ominus]}{2}$ (4) $2[\text{NO}_3^\ominus]$

16. The volume of water needed to dissolve 1 mg of PbSO_4 ($K_{sp} = 1.44 \times 10^{-8}$, M_w of $\text{PbSO}_4 = 303 \text{ g}$) at 25°C is

- (1) 80 mL (2) 43 mL
 (3) 27.5 mL (4) 10 mL

17. A student wants to prepare a saturated solution of Ag^\oplus having maximum $[\text{Ag}^\oplus]$ ion by selecting one out of three salts from:

AgCl ($K_{sp} = 2.0 \times 10^{-10}$), AgBr ($K_{sp} = 5 \times 10^{-13}$), and Ag_2CrO_4 ($K_{sp} = 2.4 \times 10^{-12}$). Which compound should be used to have maximum $[\text{Ag}^\oplus]$?

- (1) AgCl (2) AgBr
 (3) Ag_2CrO_4 (4) Any one of them

18. How many grams of KBr can be added to 1 L of 0.12 M solution of AgNO_3 just to start the precipitation of AgBr . (M_w of $\text{KBr} = 120$; K_{sp} of $\text{AgBr} = 10^{-13}$)

- (1) 10^{-10} g (2) 10^{-9} g
 (3) $0.5 \times 10^{-10} \text{ g}$ (4) $0.5 \times 10^{-9} \text{ g}$

19. The solubility of silver benzoate ($\text{C}_6\text{H}_5\text{COOAg}$) in H_2O and in a buffer solution of $\text{pH} = 2, 3$, and 4 are S_1, S_2, S_3 and S_4 respectively. The decreasing order of solubility is

- (1) $S_1 > S_2 > S_3 > S_4$ (2) $S_4 > S_3 > S_2 > S_1$
 (3) $S_2 > S_3 > S_4 > S_1$ (4) $S_3 > S_2 > S_4 > S_1$

20. The solubility of CH_3COOAg in a buffer solution with pH

$$= 4, \text{ whose } K_{sp} = 10^{-12} \text{ and } K_a = \frac{10^{-4}}{3} \text{ is}$$

- (1) 10^{-6} (2) 0.5×10^{-6}
 (3) 5×10^{-6} (4) 2×10^{-6}

21. Refer to Q. 20 above, the ratio of solubility of CH_3COOAg in a buffer solution with $\text{pH} = 4$ and in H_2O is

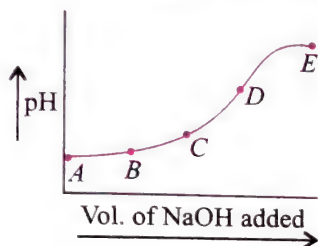
- (1) $1/2$ (2) 2 (3) $1/3$ (4) 3

22. What is the maximum molarity of Co^{+2} ions in 0.1 M HCl saturated with $0.1 \text{ M H}_2\text{S}$. ($K_a = 4 \times 10^{-21}$). Given: K_{sp} of $\text{CoS} = 2 \times 10^{-21}$.

- (1) 0.10 M (2) 1.00 M
(3) $4.48 \times 10^{-11} \text{ M}$ (4) 0.50 M

23. The following curve shows the change of pH during the course of titration of weak acid HA with a strong base. At which point in the titration curve is the concentration of acid equal to that of its conjugate base.

- (1) Point B (2) Point C (3) Point D (4) Point E



24. If the salts M_2X , QY_2 , and PZ_3 have the same solubilities

($< \frac{4}{27}$), their K_{sp} values are related

- (1) $K_{sp}(\text{M}_2\text{X}) = K_{sp}(\text{QY}_2) > K_{sp}(\text{PZ}_3)$
(2) $K_{sp}(\text{M}_2\text{X}) > K_{sp}(\text{QY}_2) = K_{sp}(\text{PZ}_3)$
(3) $K_{sp}(\text{M}_2\text{X}) = K_{sp}(\text{QY}_2) = K_{sp}(\text{PZ}_3)$
(4) $K_{sp}(\text{M}_2\text{X}) > K_{sp}(\text{QY}_2) > K_{sp}(\text{PZ}_3)$

25. Arrange the following solutions in decreasing order of $[\text{Ag}^+]$ ion:

I. $1 \text{ M } [\text{Ag}(\text{CN})_2]^\ominus$

II. Saturated AgCl

III. $1 \text{ M } [\text{Ag}(\text{NH}_3)_2]^\oplus$ in 0.1 M NH_3

IV. Saturated AgI

(K_{sp} of $\text{AgCl} = 10^{-10}$, K_{sp} of $\text{AgI} = 8.3 \times 10^{-17}$)

K_f (formation constant) $[\text{Ag}(\text{CN})_2]^\ominus = 10^{21}$,

$K_f[\text{Ag}(\text{NH}_3)_2]^\oplus = 10^8$

- (1) $\text{I} > \text{II} > \text{III} > \text{IV}$ (2) $\text{II} > \text{III} > \text{I} > \text{IV}$
(3) $\text{IV} > \text{III} > \text{II} > \text{I}$ (4) $\text{I} > \text{IV} > \text{III} > \text{II}$

ANSWERS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (1) | 2. (2) | 3. (4) | 4. (3) | 5. (1) |
| 6. (3) | 7. (2) | 8. (3) | 9. (4) | 10. (1) |
| 11. (4) | 12. (2) | 13. (4) | 14. (4) | 15. (3) |
| 16. (3) | 17. (3) | 18. (1) | 19. (3) | 20. (4) |
| 21. (2) | 22. (4) | 23. (3) | 24. (1) | 25. (2) |

Illustrations Based on Application of Equilibria (K_{sp}) to Electrochemistry and Thermodynamics

ILLUSTRATION 8.130

For galvanic cell:

$\text{Ag}|\text{AgCl(s)}, \text{KCl}(0.2 \text{ M})||\text{KBr}(0.001 \text{ M}), \text{AgBr(s)}|\text{Ag}$
Calculate EMF generated and assign correct polarity to each electrode for spontaneous process after taking into account the cell reaction at 25°C .

$$K_{sp} \text{ AgCl} = 2.8 \times 10^{-10}, K_{sp} \text{ AgBr} = 3.3 \times 10^{-13}$$

Sol.

a. LHS electrode

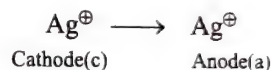
$$K_{sp} = [\text{Ag}^+][\text{Cl}^\ominus] = [\text{Ag}^+][0.2]$$

$$\text{RHS electrode } K_{sp} = [\text{Ag}^+][\text{Br}^\ominus] = [\text{Ag}^+][10^{-3}]$$

Calculate $[\text{Ag}^+]$ for each electrode and then calculate electrode potential and finally the EMF.

It is a concentration cell.

$$\therefore E^\ominus = 0$$



$$E = E^\ominus - \frac{0.59}{n} \log \frac{[\text{Ag}^\oplus]_a}{[\text{Ag}^\oplus]_c}$$

$$K_{sp} \text{ of } [\text{AgCl}] = 2.8 \times 10^{-10}$$

$$[\text{Ag}^\oplus]_a = \frac{2.8 \times 10^{-10}}{0.2} = 14 \times 10^{-10}$$

$$K_{sp} [\text{AgBr}] = 3.3 \times 10^{-13}$$

$$[\text{Ag}^\oplus]_c = \frac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10}$$

$$\begin{aligned} E &= -\frac{0.059}{1} \log \frac{14 \times 10^{-10}}{3.3 \times 10^{-10}} = -0.059 \log \left[\frac{14}{3.3} \right] \\ &= -0.059 \times 0.6276 \\ &= -0.037 \end{aligned}$$

ILLUSTRATION 8.131

At 25°C , after the addition of 110 mL of 0.1 N NaCl solution to 100 mL of 0.1 N AgNO_3 solution; the reduction potential of a silver electrode placed in it is 0.36 V . Calculate the K_{sp} of AgCl .

(Given: $E^\ominus \text{Ag/Ag}^\oplus = -0.799 \text{ V}$)

Sol. 110 mL of $0.1 \text{ N NaCl} + 100 \text{ mL}$ of 0.1 N AgNO_3
 $110 \times 0.1 = 11 \text{ mEq}$ $100 \times 0.1 = 10 \text{ mEq}$
So mEq of AgNO_3 reacts with 10 mEq of NaCl to give 10 mEq of AgCl .

$$\text{mEq of NaCl left} = 11 - 10 = 1 \text{ mEq}$$

$$\text{Total volume} = 100 + 110 = 210 \text{ mL}$$

\therefore Concentration of NaCl and

$$\therefore \text{Concentration of } [\text{Cl}^\ominus] = \frac{1 \text{ mEq}}{210 \text{ mL}} = \frac{1}{210} \text{ N or M}$$

The electrode is $\text{Cl}^\ominus, \text{AgCl}|\text{Ag}$



$$E^\ominus \text{Ag}^\oplus | \text{Ag} = 0.799 \text{ V}$$

$$\left[\begin{aligned} K_{\text{sp}} &= [\text{Ag}^\oplus][\text{Cl}^\ominus] \\ \therefore [\text{Ag}^\oplus] &= \frac{K_{\text{sp}}}{[\text{Cl}^\ominus]} \end{aligned} \right.$$

$$E_{\text{cell}} = 0.799 - 0.059 \log \frac{[\text{Cl}^\ominus]}{K_{\text{sp}}}$$

$$E_{\text{cell}} = 0.799 + \frac{0.059}{1} \log \frac{K_{\text{sp}}}{[\text{Cl}^\ominus]}$$

$$0.36 = 0.799 + 0.059 \log K_{\text{sp}} - 0.59 \log [\text{Cl}^\ominus]$$

$$0.36 = 0.799 + 0.059 \log K_{\text{sp}} - 0.059 \log \frac{1}{210}$$

$$0.059 \log K_{\text{sp}} = 0.36 - 0.799 + 0.059 \log \frac{1}{210} = -0.576$$

$$\log K_{\text{sp}} = -\frac{0.576}{0.059} = -9.76$$

$$\therefore K_{\text{sp}} = 1.73 \times 10^{-10}$$

ILLUSTRATION 8.132

Calculate the entropy of OH^\ominus ion at 298 K. Given:

a. $\text{H}_2\text{O} \rightleftharpoons \text{H}^\oplus + \text{OH}^\ominus$ ($\Delta H = 13.4 \text{ kcal}$)

b. K_{eq} for the reaction = 10^{-14} .

c. $S^\ominus(\text{H}^\oplus) = 0.0$

d. $S^\ominus(\text{H}_2\text{O}) = 16.7 \text{ cal/mol K}$.

Sol. $\Delta G^\ominus = -2.30RT \log K_{\text{eq}}$
 $= -2.3 \times 2 \times 10^{-3} \times 298 \log (10^{-14})$
 $= 19191.2 \text{ cal} = 19.1 \text{ kcal mol}^{-1}$

$$\Delta S^\ominus = \frac{\Delta H^\ominus - \Delta G^\ominus}{T} = \frac{(13.4 - 19.1) \times 10^3}{298}$$

$$= -19.2 \text{ cal mol}^{-1}$$

$$\Delta S^\ominus = S^\ominus(\text{H}^\oplus) + S^\ominus(\text{OH}^\ominus) - S^\ominus(\text{H}_2\text{O})$$

$$-19.2 = 0.0 + S^\ominus(\text{OH}^\ominus) - 16.7$$

$$\therefore S^\ominus(\text{OH}^\ominus) = -2.5 \text{ cal mol}^{-1} \text{ K}^{-1}$$

ILLUSTRATION 8.133

Calculate K_{sp} for AgCl. Given:

$$\Delta_f H^\ominus \text{Ag}^\oplus = 25.3 \text{ kcal mol}^{-1}$$

$$\Delta_f H^\ominus \text{Cl}^\ominus = -40.0 \text{ kcal mol}^{-1}$$

$$\Delta_f H^\ominus \text{AgCl} = -30.36 \text{ kcal mol}^{-1}$$

$$S^\ominus \text{Ag}^\oplus, S^\ominus \text{Cl}^\ominus, \text{ and } S^\ominus \text{AgCl} \text{ are } 17.7, 13.2, \text{ and } 23.0 \text{ cal mol}^{-1}.$$

Sol. The process is represented by:



$$\Delta H^\ominus = \Delta_f H^\ominus(\text{Ag}^\oplus) + \Delta_f H^\ominus(\text{Cl}^\ominus) - \Delta_f H^\ominus(\text{AgCl})$$

$$= 25.3 + (-40.0) - (-30.36) = 15.7 \text{ kcal mol}^{-1}.$$

$$\Delta S^\ominus = S^\ominus(\text{Ag}^\oplus) + S^\ominus(\text{Cl}^\ominus) - S^\ominus(\text{AgCl})$$

$$= 17.7 + 13.2 - 23.0 = 7.9 \text{ cal mol}^{-1}$$

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus = 15.7 \times 10^3 - (298)(7.9)$$

$$= 13350 \text{ cal}$$

$$\Delta G^\ominus = -2.30RT \log K.$$

$$\therefore -\log K = \frac{\Delta G^\ominus}{2.30RT} = \frac{13350}{(2.30)(1.99)(298)} = 9.79$$

$$\therefore K = \text{Antilog}(-9.79) = \text{Antilog}(-9 - 0.79 + 1 - 1)$$

$$= \text{Antilog}(\overline{10.21}) = 1.6 \times 10^{-10}$$

The tabulated value of K_{sp} of AgCl = 1×10^{-10}

Solved Examples**EXAMPLE 8.1**

K_a for HA is 4.9×10^{-8} . After making the necessary approximation, calculate for its decimolar solution,

- a. % dissociation b. OH^\ominus concentration c. pH

Sol. $\alpha = \sqrt{K_a/C} = \sqrt{\frac{(4.9 \times 10^{-8})}{1/10}} \quad \left(C = \frac{1}{10} \text{ N or M} \right)$

$$= 7 \times 10^{-4} = 0.07\% \quad (K_a = 4.9 \times 10^{-8})$$

$$K_a = 4.9 \times 10^{-8} = 7 \times 10^{-4} = 0.07\%$$

$$[\text{H}^\oplus] = Ca = 1/10 \times 7 \times 10^{-4} = 7 \times 10^{-5}$$

$$\therefore \text{pH} = 4.15 \quad [\text{OH}^\ominus] [\text{H}^\oplus] = 10^{-14}$$

$$[\text{OH}^\ominus] = \frac{10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10}$$

EXAMPLE 8.2

Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its percent dissociation in a solution which contains 0.10 moles of nicotinic acid per 2.0 L of solution.

Sol. Given, $\text{HNiC} \rightleftharpoons \text{H}^\oplus + \text{NiC}^\ominus$

1	0	0
$1 - \alpha$	α	α

Also,

$$C = 0.1/2 = 5 \times 10^{-2} \text{ mol L}^{-1}, K_a = 1.4 \times 10^{-5}$$

$$\therefore K_a = \frac{C\alpha^2}{(1 - \alpha)} = C\alpha^2$$

$$\alpha = \sqrt{K_a/C} = \sqrt{\frac{1.4 \times 10^{-5}}{5 \times 10^{-2}}} = 1.67 \times 10^{-2} \text{ or } 1.67\%$$

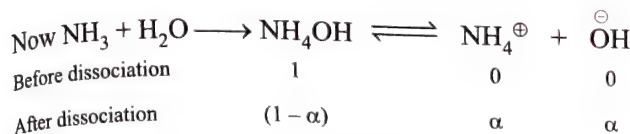
EXAMPLE 8.3

An aqueous solution contains 10% ammonia by mass and has a density of 0.99 g cm^{-3} . Calculate hydroxyl and hydrogen ion concentration in this solution K_a for $\text{NH}_4^\oplus = 5.0 \times 10^{-10} \text{ M}$.

Sol. Given, $\frac{\text{Weight of NH}_3}{\text{Weight of solution}} = 10/100$

100 g solution contains 10 gm NH_3

$$M_{\text{NH}_3} = (10 \times 1000) (17 \times (100/0.99)) \\ = 5.82 \text{ (V = mass/density)}$$



$$\therefore [\text{OH}^{\ominus}] = C\alpha = C\sqrt{(K_b/C)} = \sqrt{(K_b C)}$$

$$[C = 5.82 \text{ M and } K_b = K_w/K_a = 10^{-14}/(5 \times 10^{-10}) = 2 \times 10^{-5}]$$

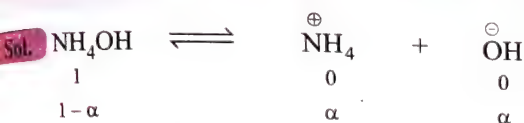
$$[\text{OH}^{\ominus}] = \sqrt{2 \times 10^{-5} \times 5.82} = 1.07 \times 10^{-2} \text{ M}$$

$$\therefore [\text{H}^{\oplus}] = 10^{-14}/1.07 \times 10^{-2} = 0.9268 \times 10^{-12} \text{ M}$$

$$\therefore \text{pH} = -\log [\text{H}^{\oplus}] = -\log 0.9268 \times 10^{-12} \text{ M} = 12.033$$

EXAMPLE 8.4

Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of $\text{pH} = 11$.



Given $\text{pH} = 11$

$$\therefore [\text{H}^{\oplus}] = 10^{-11}, \therefore [\text{OH}^{\ominus}] = 10^{-3} = C\alpha$$

Since, $C = 0.05$

$$\therefore \alpha = 10^{-3}/C = 10^{-3}/0.05 = 2 \times 10^{-2} = 2\%$$

EXAMPLE 8.5

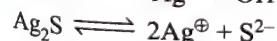
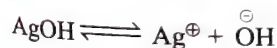
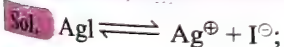
Three suggestion are made for ways to remove silver ions from solution:

- Make the solution 0.01 M in NaI.
- Buffer the solution at pH 13.
- Make the solution 0.001 M Na_2S .

What will be the equilibrium silver ion concentration in each case? Which course of action is most effective in removing Ag^{\oplus} ions?

$$K_{\text{sp}}(\text{AgI}) = 8.5 \times 10^{-17}; K_{\text{sp}}(\text{AgOH}) = 2 \times 10^{-8};$$

$$K_{\text{sp}}(\text{Ag}_2\text{S}) = 5.5 \times 10^{-51}$$



$$\text{a. } [\text{Ag}^{\oplus}] = \frac{8.5 \times 10^{-17}}{10^{-2}} = 8.5 \times 10^{-15} \text{ M}$$

$$\text{b. } \text{pH} = 13 \therefore [\text{H}^{\oplus}] = 10^{-13}; [\text{OH}^{\ominus}] = 10^{-1}$$

$$[\text{Ag}^{\oplus}] = \frac{2 \times 10^{-8}}{10^{-1}} = 2 \times 10^{-7} \text{ M}$$

$$\text{c. } [\text{Ag}^{\oplus}] = \sqrt{\frac{5.5 \times 10^{-51}}{10^{-3}}} = 2.345 \times 10^{-24} \text{ M}$$

(c) is most effective since $[\text{Ag}^{\oplus}]$ is the least in this case.

EXAMPLE 8.6

Calculate the the ratio of conjugate base/ weak acid required to prepare an aqueous solution of benzoic acid and sodium benzoate with pH of 4.5. The acid dissociation constant of benzoic acid is 6.5×10^{-5} .



$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{COOH}^{\ominus}]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\begin{aligned} \log \frac{[\text{C}_6\text{H}_5\text{COOH}^{\ominus}]}{[\text{C}_6\text{H}_5\text{COOH}]} &= \text{pH} - \text{p}K_a \\ &= 4.5 - (-\log 6.5 \times 10^{-5}) \\ &= (4.5 - 4.187) = 0.3129 \end{aligned}$$

$$\frac{[\text{C}_6\text{H}_5\text{COO}^{\ominus}]}{[\text{C}_6\text{H}_5\text{COOH}]} = \text{Antilog}(0.3129) = 2.055 \approx 2$$

EXAMPLE 8.7

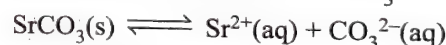
A solution is saturated with respect to SrF_2 $K_{\text{sp}} = 7.9 \times 10^{-10}$ and SrCO_3 , $K_{\text{sp}} = 7.0 \times 10^{-10}$. If the fluoride ion concentration is found to be $4.0 \times 10^{-2} \text{ M}$. What is the concentration of carbonate ions?



$$K_{\text{sp}} = [\text{Sr}^{2+}] [\text{F}^{\ominus}]^2$$

$$[\text{Sr}^{2+}] = \frac{K_{\text{sp}}}{[\text{F}^{\ominus}]^2} = \frac{7.9 \times 10^{-10}}{(4.0 \times 10^{-2})^2} = 4.938 \times 10^{-7} \text{ M}$$

This concentration of Sr^{2+} ions should also satisfy the other equilibrium expression for SrCO_3

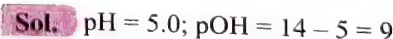


$$K_{\text{sp}} = [\text{Sr}^{2+}] [\text{CO}_3^{2-}]$$

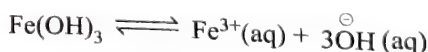
$$[\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Sr}^{2+}]} = \frac{7.0 \times 10^{-10}}{4.938 \times 10^{-7}} = 1.4 \times 10^{-3}$$

EXAMPLE 8.8

Compare the solubilities of $\text{Fe}(\text{OH})_3$ ($K_{\text{sp}} = 4 \times 10^{-38}$) and $\text{Ni}(\text{OH})_2$ ($K_{\text{sp}} = 2 \times 10^{-16}$) at $\text{pH} = 5.0$



$$[\text{OH}^{\ominus}] = -\text{Antilog } 9.0 = 1 \times 10^{-9} \text{ M}$$



$$[\text{Fe}^{3+}] [\text{OH}^{\ominus}]^3 = K_{\text{sp}} = 4 \times 10^{-38}$$

$$[\text{Fe}^{3+}] = S = \frac{4 \times 10^{-38}}{(1.8 \times 10^{-9})^3} = 4 \times 10^{-11} \text{ M}$$

Ni^{2+} ions can be present in high concentration in solution and do not precipitate. Let $[\text{Ni}^{2+}]$ be 1M

$$[\text{Ni}^{2+}] [\text{OH}^{\ominus}]^2 = (1)^2 (\pm 10^{-9})^2 < 1 \times 10^{-18} < K_{\text{sp}}$$

EXAMPLE 8.9

What is the pH at which 0.01 M Co^{2+} ions in solution precipitate down as $\text{Co}(\text{OH})_2$? (K_{sp} of $\text{Co}(\text{OH})_2$ is 2.5×10^{-16})



$$[\text{Co}^{2+}][\text{OH}]^2 = K_{\text{sp}} = 2.5 \times 10^{-16}$$

$$(0.01)[\text{OH}]^2 = 2.5 \times 10^{-16}$$

$$[\text{OH}]^2 = \frac{2.5 \times 10^{-16}}{0.01} = 2.5 \times 10^{-14}$$

$$[\text{OH}] = \sqrt{2.5 \times 10^{-14}} = 1.58 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log 1.58 \times 10^{-7} = 6.8$$

$$\text{pH} + \text{pOH} = 14 \text{ and } \text{pH} = 14 - \text{pOH} = 14 - 6.8 = 7.2$$

EXAMPLE 8.10

A buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 mol/L of NH_4OH is in equilibrium with Al^{3+} and Mg^{2+} ions. Calculate $[\text{Al}^{3+}]$ and $[\text{Mg}^{2+}]$ in solution.

Given:

$$K_b(\text{NH}_4\text{OH}) = 2.0 \times 10^{-5}; K_{\text{sp}}[\text{Mg}(\text{OH})_2] = 6.0 \times 10^{-12}; K_{\text{sp}}[\text{Al}(\text{OH})_3] = 6 \times 10^{-32}$$

Sol. At equilibrium, $[\text{OH}^-]$ will determine the concentration of metal ions in solution.

First calculate $[\text{OH}^-]$ in the solution using basic buffer equation.

$$[\text{OH}^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]} = 2 \times 10^{-5} \times \frac{0.05}{0.25} = 4 \times 10^{-6} \text{ M}$$

Note:

It is easy to calculate $[\text{OH}^-]$ using $[\text{OH}^-] = \frac{K_b [\text{Base}]}{[\text{Salt}]}$

as compared to $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

Now this controls the following equilibria:



$$\Rightarrow [\text{Mg}^{2+}] = \frac{6.0 \times 10^{-12}}{(4 \times 10^{-6})^2} = 0.375 \text{ M}$$



$$[\text{Al}^{3+}] = \frac{6 \times 10^{-32}}{(4 \times 10^{-6})^3} = 9.37 \times 10^{-16} \text{ M}$$

EXAMPLE 8.11

Determine the mass of PbI_2 that will dissolve in (a) 500 mL water (b) 500 mL of 0.10 M KI solution (c) 500 mL of a solution containing 1.33 g $\text{Pb}(\text{NO}_3)_2$, K_{sp} of $\text{PbI}_2 = 1.4 \times 10^{-8}$.



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2 = 1.4 \times 10^{-8}$$

a. Let $x = [\text{Pb}^{2+}]$, then $[\text{I}^-] = 2x$

$$\therefore 4x^3 = 1.4 \times 10^{-8}; x = 1.5 \times 10^{-3} \text{ M}$$

Number of moles is 500 mL H_2O

$$= \frac{1.5 \times 10^{-3} \times 500}{1000} = 0.75 \times 10^{-3} \text{ mol}$$

$$\text{Mass of } \text{PbI}_2 = 0.75 \times 10^{-3} \times 461 = 0.35 \text{ g}$$

b. $[\text{Pb}^{2+}][\text{I}^-]^2 = 1.4 \times 10^{-8}$

$$\therefore [\text{Pb}^{2+}] = 1.4 \times 10^{-6} \text{ M}$$

Mass of PbI_2 is 500 mL of 0.1 M KI solution

$$= 1.4 \times 10^{-6} \text{ M} \times 0.5 \text{ L} \times 461 \text{ g mol}^{-1}$$

$$= 3.2 \times 10^{-4} \text{ g} = 0.32 \text{ mg}$$

c. Molarity of $\text{Pb}(\text{NO}_3)_2$

$$= \frac{W_2 \times 1000}{Mw_2 \times V_{\text{Sol}}} = \frac{1.33 \times 1000}{331 \times 500} = 8.04 \times 10^{-3} \text{ M}$$

If the concentration of PbI_2 is y , then $[\text{I}^-] = 2y$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$$

$$1.4 \times 10^{-8} = (8.04 \times 10^{-3})(2y)^2$$

$$\therefore y = 6.6 \times 10^{-4} \text{ M}$$

Mass of PbI_2 in 500 mL of a solution of 1.33 g of $\text{Pb}(\text{NO}_3)_2$

$$= 6.6 \times 10^{-4} \times 0.5 \text{ L} \times 461 = 0.15 \text{ g}$$

EXAMPLE 8.12

Should a precipitate of barium fluoride be obtained when 100 mL of 0.25 M NaF and 100 mL of 0.015 M $\text{Ba}(\text{NO}_3)_2$ are mixed.

$$K_{\text{sp}} \text{ of } \text{BaF}_2 = 1.7 \times 10^{-6}$$



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2 = 1.7 \times 10^{-6}$$

$$[\text{F}^-] = \frac{100 \text{ mL} \times 0.25 \text{ M}}{200 \text{ mL}} = 0.125 \text{ M} \text{ and}$$

$$[\text{Ba}^{2+}] = \frac{100 \text{ mL} \times 0.015 \text{ M}}{200 \text{ mL}} = 0.0075 \text{ M}$$

Ionic product of BaF_2

$$\text{IP} = [\text{Ba}^{2+}][\text{F}^-]^2 = (7.5 \times 10^{-3})(0.125)^2 = 1.2 \times 10^{-4}$$

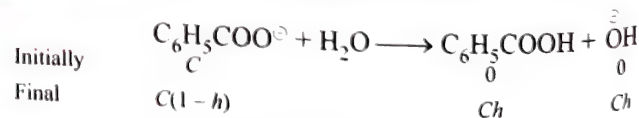
Since ionic product $> K_{\text{sp}}$

\therefore Precipitation occur

EXAMPLE 8.13

A saturated solution of silver benzoate, AgOCC_6H_5 has a pH of 8.63, K_a for benzoic acid is 6.5×10^{-5} . Estimate K_{sp} for silver benzoate.

Sol. First method: $\text{pH} = 8.63$, $\text{pOH} = 5.37$, $[\text{OH}^-] = 4.3 \times 10^{-6}$



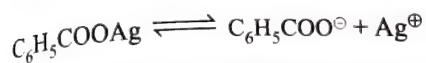
$$K_h = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]}, \quad \text{Ch} = 4.3 \times 10^{-6}$$

$$\therefore [\text{C}_6\text{H}_5\text{COO}^-] = \frac{(4.3 \times 10^{-6})(4.3 \times 10^{-6})}{K_h} \quad \dots(i)$$

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{6.5 \times 10^{-5}}$$

Substituting the value of K_h in equation (i)

$$\therefore [\text{C}_6\text{H}_5\text{COO}^\ominus] = \frac{(4.3 \times 10^{-6})^2 \times (6.5 \times 10^{-5})}{10^{-14}}$$



$$K_{sp} = [\text{Ag}^\oplus][\text{C}_6\text{H}_5\text{COO}^\ominus] = (0.12)^2 = 1.4 \times 10^{-2}$$

Second method:

Use formula for the pH of salt of S_B/W_A

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C)$$

$$8.63 = \frac{1}{2}(14 + 4.187 + \log C)$$

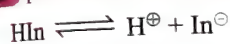
$$\therefore C = 0.12$$

$$K_{sp} = [\text{Ag}^\oplus][\text{C}_6\text{H}_5\text{COO}^\ominus] = (0.12)^2 = 1.4 \times 10^{-2}$$

EXAMPLE 8.14

For the indicator 'HIn' the ratio $(\text{Ind}^\ominus)/(\text{HIn})$ is 7.0 at pH of 4.3. What is K_{eq} for the indicator?

Sol. $\text{pH} = 4.3$, $[\text{H}^\oplus] = 5.0 \times 10^{-5} \text{ M}$

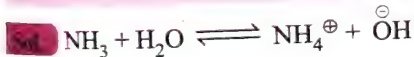


$$K_{eq} = \frac{[\text{H}^\oplus][\text{Ind}^\ominus]}{[\text{HIn}]}$$

$$= (5.0 \times 10^{-5})(7.0) = 3.5 \times 10^{-4} \text{ M}$$

EXAMPLE 8.15

Determine $[\text{OH}^\ominus]$ of a 0.050 M solution of ammonia to which sufficient NH_4Cl has been added to make the total $[\text{NH}_4^\oplus]$ equal to 0.1 M.



$$K_b = \frac{[\text{NH}_4^\oplus][\text{OH}^\ominus]}{[\text{NH}_3]} = \frac{(0.1)x}{(0.050)} = 1.8 \times 10^{-5} \text{ thus}$$

$$x = [\text{OH}^\ominus] = 9.0 \times 10^{-6}$$

EXAMPLE 8.16

K_{sp} of AgCl is 2.8×10^{-10} at 25°C . Calculate solubility of AgCl in.

a. Pure water

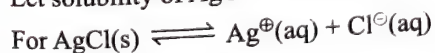
b. 0.1 M AgNO_3

c. 0.1 M KCl or 0.1 M NaCl

Sol.

a. **In pure water:**

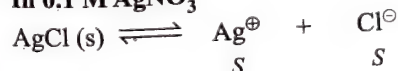
Let solubility of AgCl be $S \text{ mol L}^{-1}$



$$K_{sp} = [\text{Ag}^\oplus][\text{Cl}^\ominus] = S \times S$$

$$\therefore S = \sqrt{K_{sp}} = \sqrt{(2.8 \times 10^{-10})} = 1.673 \times 10^{-5} \text{ mol L}^{-1}$$

b. **In 0.1 M AgNO_3**

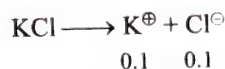
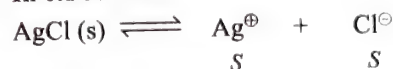


$$\therefore K_{sp} = [\text{Ag}^\oplus][\text{Cl}^\ominus] = (0.1 + S)(S)$$

($S \ll 0.1$, presence of common ion decreases solubility)

$$\therefore S(0.1) = 2.8 \times 10^{-10} \therefore S = 2.8 \times 10^{-9} \text{ M}$$

c. **In 0.1 M KCl**



$$K_{sp} = [\text{Ag}^\oplus][\text{Cl}^\ominus] = (S)(S + 0.1) \quad (S \ll 0.1 \text{ M})$$

$$\therefore S(0.1) = 2.8 \times 10^{-10}$$

$$S = 2.8 \times 10^{-9} \text{ M}$$

Alternative method for (b) and (c):

$$\text{For (b) and (c), } S_{\text{new}} = \frac{K_{sp}}{(C)^n} = \frac{2.8 \times 10^{-10}}{(0.1)^1} = 2.8 \times 10^{-9} \text{ M}$$

where C = conc. of the common ion added

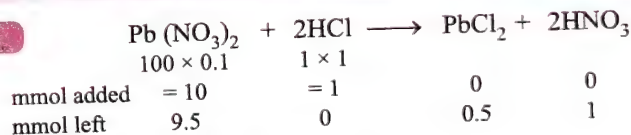
n = number of common ion in AgCl

In (b) Ag^\oplus and in (c) Cl^\ominus are the common ion.

EXAMPLE 8.17

K_{sp} of PbCl_2 is 10^{-13} . What will be $[\text{Pb}^{2+}]$ in a solution prepared by mixing 100 mL of 0.1 M $\text{Pb}(\text{NO}_3)_2$ and 1.0 mL 1 M HCl ?

Sol.



Since HCl is a limiting reagent:

$$\text{Concentration} = \frac{\text{mmol}}{\text{Total volume}} \therefore [\text{Pb}^{2+}] = \frac{9.5 + 0.5}{101}$$

Now if PbCl_2 is precipitated, then contribution 0.5 M of $[\text{Pb}^{2+}]$ from PbCl_2 should be left.

To see precipitation, ionic product $> K_{sp}$

$$\begin{aligned} \text{Ionic product} &= [\text{Pb}^{2+}][\text{Cl}^\ominus]^2 \\ &= [10/101][1/101]^2 = 9.70 \times 10^{-6} \end{aligned}$$

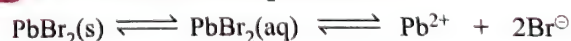
Which is greater than K_{sp} of PbCl_2 and thus, precipitation of PbCl_2 occurs.

$$[\text{Pb}^{2+}] = \frac{9.5}{101} = 9.4 \times 10^{-2} \text{ mole litre}^{-1}$$

EXAMPLE 8.18

K_{sp} of PbBr_2 is 8×10^{-5} . If the salt is 80% dissociated in solution, calculate the solubility of salt in g L^{-1} .

Sol. Let solubility of PbBr_2 be $S \text{ mol L}^{-1}$



$$\begin{array}{cc} \frac{S \times 80}{100} & \frac{2S \times 80}{100} \end{array}$$

Ionisation of $\text{PbBr}_2(\text{s}) = 80\%$

$$\therefore K_{sp} = [\text{Pb}^{2+}][\text{Br}^\ominus]^2$$

$$8 \times 10^{-5} = \left(\frac{S \times 80}{100} \right) \left(\frac{2S \times 80}{100} \right)^2$$

$$\therefore S = 0.034 \text{ mol L}^{-1} \text{ (M.wt of PbBr}_2 = 367)$$

$$S = 0.034 \times 367 \text{ g L}^{-1} = 12.48 \text{ g L}^{-1}$$

EXAMPLE 8.19

Equal volumes of 0.02 M CaCl_2 and 0.0004 M Na_2SO_4 are mixed. Will a precipitate form? (K_{sp} for $\text{CaSO}_4 = 2.4 \times 10^{-5}$)



Milli moles 0.02V 0.0004V 0 0

Suppose V ml of both are mixed

$$\therefore [\text{Ca}^{2+}] = \frac{0.02V}{2V} = 10^{-2} \text{ M},$$

$$[\text{SO}_4^{2-}] = \frac{0.0004V}{2V} = 2 \times 10^{-4} \text{ M}$$

Thus, $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ in solution $< K_{\text{sp}}$

$$2 \times 10^{-6} < 2.4 \times 10^{-5}$$

$\therefore \text{CaSO}_4$ will not precipitate

EXAMPLE 8.20

A solution containing both Zn^{2+} and Mn^{2+} ions at a concentration of 0.01 M is saturated with H_2S . What is pH at which MnS will form a ppt? Under these conditions what will be the concentration of Zn^{2+} ions remaining in the solution? Given that K_{sp} of ZnS is 10^{-22} and K_{sp} of MnS is 5.6×10^{-16} , $K_1 \times K_2$ of $\text{H}_2\text{S} = 1.10 \times 10^{-21}$.

Sol. The minimum $[\text{S}^{2-}]$ for the start of the precipitation is that which satisfies the K_{sp} of MnS is in which $[\text{Mn}^{2+}] = 0.01 \text{ M}$

$$[\text{S}^{2-}] = \frac{K_{\text{sp}} \text{ of MnS}}{[\text{Mn}^{2+}]} = \frac{5.6 \times 10^{-16}}{0.01} = 5.6 \times 10^{-14}$$

The $[\text{H}^{\oplus}]$ of the soln. having the above $[\text{S}^{2-}]$ can be calculated from the H_2S dissociation eq. expression.

$$\frac{[\text{H}^{\oplus}]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{[\text{H}^{\oplus}]^2 \times 5.6 \times 10^{-14}}{0.01} = 1.1 \times 10^{-21}$$

$$\therefore [\text{H}^{\oplus}] = 4.43 \times 10^{-5} \text{ and pH} = 4.35$$

If the $[\text{H}^{\oplus}]$ is greater than $4.43 \times 10^{-5} \text{ M}$ than the $[\text{S}^{2-}]$ will be less than $5.6 \times 10^{-14} \text{ M}$ and MnS will no longer ppt. from the soln. Therefore, the conc of Zn^{2+} ion remaining in the soln. can be calculated from the K_{sp} of ZnS .

$$\therefore [\text{Zn}^{2+}] = \frac{K_{\text{sp}} \text{ of ZnS}}{[\text{S}^{2-}]} = \frac{1.0 \times 10^{-22}}{5.6 \times 10^{-14}} = 1.79 \times 10^{-9} \text{ M}$$

Thus, by properly adjusting the $[\text{H}^{\oplus}]$ in the soln. it is possible to precipitate effectively all of the Zn from the solution without precipitation any Mn^{2+} ion.

EXAMPLE 8.21

A sample of hard water contains 0.005 mol of CaCl_2 per litre. What is the minimum concentration of Na_2SO_4 , which must be added for removing Ca^{2+} ions from this water sample? (K_{sp} for CaSO_4 is 2.4×10^{-5} at 25°C)



$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$$

Let $[\text{SO}_4^{2-}] = a$, just sufficient to precipitate CaSO_4 from a solution having $[\text{Ca}^{2+}] = 0.005 \text{ M}$

$$\text{The } [0.005][a] = 2.4 \times 10^{-5}$$

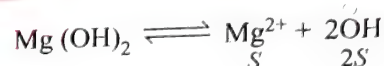
$$\therefore a = \frac{2.4 \times 10^{-5}}{0.005}$$

$$[\text{SO}_4^{2-}] = 4.8 \times 10^{-3} \text{ mol L}^{-1}$$

EXAMPLE 8.22

Calculate pH of saturated solution of $\text{Mg}(\text{OH})_2$, K_{sp} for $\text{Mg}(\text{OH})_2$ is 8.9×10^{-12} .

Sol. Let solubility of $\text{Mg}(\text{OH})_2$ be $S \text{ mol L}^{-1}$



$$\therefore [\text{Mg}^{2+}][\text{OH}^-]^2 = K_{\text{sp}}$$

$$4s^3 = 8.9 \times 10^{-12} \quad \therefore s = 1.305 \times 10^{-4} \text{ M}$$

$$\therefore [\text{OH}^-] = 2 \times 1.305 \times 10^{-4} \text{ M}$$

$$\therefore \text{pOH} = 3.5832 \text{ and pH} = 10.4168$$

EXAMPLE 8.23

0.1 milli moles of CdSO_4 are present in 10 ml acid solution of 0.08 N HCl . Now H_2S is passed to precipitate all the Cd^{2+} ions. What would be the pH of solution after filtering off precipitate, boiling of H_2S and making the solution 100 ml by adding H_2S ?



mmol added \Rightarrow 0.1 10 \times 0.08

mmol after reaction \Rightarrow 0 = 0.8 0.1 0.1

$$\text{mmoles of H}^{\oplus} = [\text{From HCl}] + [\text{From H}_2\text{SO}_4]$$

$$= 0.8 + 0.1 \times 2 = 1.0$$

$$\text{Total volume} = 100 \text{ mL}$$

$$\therefore [\text{H}^{\oplus}] = 1/100 = 10^{-2} \text{ M} \quad \therefore \text{pH} = 2$$

EXAMPLE 8.24

The solubility of $\text{Mg}(\text{OH})_2$ is increased by the addition of NH_4^{\oplus} ion. Calculate

a. K_c for the reaction:



$$K_{\text{sp}} \text{ of } \text{Mg}(\text{OH})_2 = 6 \times 10^{-12}, K_b \text{ of } \text{NH}_3 = 1.8 \times 10^{-5}.$$

b. Find the solubility of $\text{Mg}(\text{OH})_2$ in a solution containing 0.5 M NH_4Cl before addition of $\text{Mg}(\text{OH})_2$.

Sol. $K_c = \frac{[\text{NH}_3]^2 [\text{Mg}^{+2}]}{[\text{NH}_4^{\oplus}]^2} = \frac{[\text{NH}_4\text{OH}]^2 [\text{Mg}^{+2}]}{[\text{NH}_4^{\oplus}]^2} \quad \dots(i)$

Also,



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots(\text{ii})$$

$$\therefore K_c \times K_b^2 = [\text{Mg}^{2+}][\text{OH}^-]^2 = K_{\text{sp}} \text{ of Mg(OH)}_2$$

$$\therefore K_c = \frac{K_{\text{sp}}}{K_b^2} = \frac{6 \times 10^{-12}}{(1.8 \times 10^{-5})^2} = 1.85 \times 10^{-2}$$

Let a mol L⁻¹ of Mg(OH)₂ be dissolved in presence of 0.5 M NH₄Cl



$$\text{Moles before reaction} \Rightarrow \quad 0.5 \quad \quad 0 \quad \quad - \quad \quad 0$$

$$\text{Moles after reaction} \Rightarrow \quad (0.5 - 0.2a) \quad \quad 2a \quad \quad - \quad \quad a$$

$$\therefore K_c = \frac{a \times (2a)^2}{(0.5 - 2a)^2}$$

$$1.85 \times 10^{-12} = \frac{4a^3}{(0.5 - 2a)^2} \quad \dots(\text{iii})$$

Solving cubic equation,

$$\therefore a = 0.081 \text{ M}$$

Note: If cubic equation is not solved, then neglecting 2a in comparison to 0.5, then 'a' becomes equal to 0.1049 M.

EXAMPLE 8.25

K_{sp} of SrF₂ = 2.8×10^{-9} at 25°C. How much NaF should be added to 100 mL of solution having 0.016 M in Sr²⁺ ions to reduce its concentration to 2.5×10^{-3} M?

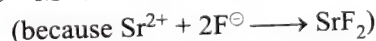
Sol. Initial [Sr²⁺] = 16×10^{-3} M

$$\text{Left [Sr}^{2+}] = 16 \times 10^{-3} \text{ M}$$

$$[\text{Sr}^{2+}] \text{ ppted} = (16 - 2.5) \times 10^{-3} = 13.5 \times 10^{-3} \text{ M}$$

[F⁻] needed for this precipitation

$$\Rightarrow 2 \times 13.5 \times 10^{-3} \text{ M} = 27.0 \times 10^{-3} \text{ M}$$



$$\text{Also } [\text{Sr}^{2+}][\text{F}^-]^2 = K_{\text{spSrF}_2} = 2.8 \times 10^{-9}$$

$$[\text{F}^-]^2 = \frac{2.8 \times 10^{-9}}{2.5 \times 10^{-3}}$$

$\therefore [\text{F}^-] = 1.058 \times 10^{-3} \text{ M}$, i.e., the concentration of F⁻ which will also appear in solution state.

$$\text{Thus, } [\text{F}^-] \text{ needed} = [27.0 + 1.058] \times 10^{-3} \text{ M} = 28.058 \times 10^{-3} \text{ M}$$

$$\therefore \text{NaF needed for 1 L} = 28.058 \times 10^{-3} \times 42 \text{ g}$$

$$\therefore \text{NaF needed for 100 mL}$$

$$= \frac{28.058 \times 10^{-3} \times 42}{10} \text{ g}$$

$$= 0.1178 \text{ g}$$

EXAMPLE 8.26

Calculate the degree of hydrolysis and pH of 0.2 M solution of NH₄Cl. Given K_b for NH₄OH is 1.8×10^{-5} .

Sol.



$$\begin{array}{cccc} \text{Before hydrolysis} & 1 & 0 & 0 \\ \text{After hydrolysis} & 1-h & h & h \end{array}$$

where h is the degree of hydrolysis.

$$\begin{aligned} h &= \sqrt{(K_h/C)} = \sqrt{(K_w/K_b \cdot C)} \\ &= \sqrt{(10^{-14})/(1.8 \times 10^{-5} \times 0.2)} = 5.27 \times 10^{-5} \end{aligned}$$

From HCl, a strong acid

$$\begin{aligned} \therefore [\text{H}^+] &= C \cdot h = C \sqrt{(K_h/C)} = \sqrt{(K_h \cdot C)} \\ &= \sqrt{(K_w \cdot C / K_b)} \\ &= \sqrt{\frac{10^{-14} \times 0.2}{1.8 \times 10^{-5}}} = 1.054 \times 10^{-5} \end{aligned}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log (1.054 \times 10^{-5}) = 4.9771$$

EXAMPLE 8.27

Calculate for 0.01 N solution of sodium acetate,

a. Hydrolysis constant b. Degree of hydrolysis

c. pH Given $K_a = 1.9 \times 10^{-5}$

Sol. for



$$\begin{array}{cccc} \text{Before hydrolysis} & 1 & 0 & 0 \\ \text{After hydrolysis} & 1-h & h & h \end{array}$$

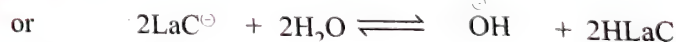
$$\text{a. } \therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$\text{b. } h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-4}$$

$$\begin{aligned} \text{c. } [\text{OH}^-] &\text{ from NaOH, a strong alkali} = Ch \\ &\therefore = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6} \text{ M} \\ &\therefore \text{pOH} = 5.64 \text{ and } \text{pH} = 8.36 \end{aligned}$$

EXAMPLE 8.28

Calcium lactate is salt of weak acid and represented as Ca(LaC)₂. A saturated solution of Ca(LaC)₂ contains 0.13 mol of salt in 0.50 L solution. The pOH of this is 5.60. Assuming complete dissociation of salt, calculate K_a of lactic acid.



$$\begin{array}{cccc} \text{Before hydrolysis} \Rightarrow & 1 & 0 & 0 \\ \text{After hydrolysis} \Rightarrow & 1-h & h & h \end{array}$$

$$\therefore [\text{Ca(LaC)}_2] = 0.13/0.5 = 0.26 \text{ M}$$

$$\therefore [\text{LaC}^-] = 0.26 \times 2 = 0.52 \text{ M}$$

[because 1 mole Ca(LaC)₂ gives 2 mole (LaC⁻)]

$$\text{Now } [\text{OH}^-] = C \cdot h = \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{(K_h \cdot C)} = \sqrt{\frac{K_w \cdot C}{K_a}}$$

where C is concentration of anion which undergoes hydrolysis.

$$\therefore 10^{-5.60} = \sqrt{\left(\frac{10^{-14} \times 0.52}{K_a}\right)} \quad K_a = 8.25 \times 10^{-4}$$

Second Method

Use direct formula for the pH of salt of W_A/S_B .

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$$

(concentration of salt = $2 \times 0.26 \text{ M}$)

$$8.4 = \frac{1}{2} (14 + \text{p}K_a + \log 2 \times 0.26)$$

$$\text{Solve for } \text{p}K_a, \therefore K_a = 8.25 \times 10^{-4}$$

EXAMPLE 8.29

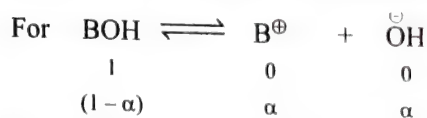
The vapour pressure of 0.01 molal solution of weak base BOH in water at 20°C is 17.536 mm. Calculate K_b for base. Aqueous tension at 20°C is 17.540 mm. Assume molality and molarity same.

Sol. We have from Raoult's law

$$\frac{p^0 - P_s}{p^0} = x_2 = \frac{17.54 - 17.536}{17.54} = 0.00022$$

$$m = \frac{x_2 \times 1000}{x_1 \times M_{W_1}} = \frac{0.00022 \times 1000}{0.999 \times 18} = 1.267 \times 10^{-2}$$

$$\text{Molality} = \text{Concentration of } [\text{BOH}] = 1.267 \times 10^{-2}$$



Molality is also given as 1×10^{-2} .

$$\therefore \frac{\text{Exp. value of molality}}{\text{Normal value of molality}} = 1 + \alpha$$

$$\therefore \frac{1.267 \times 10^{-2}}{1 \times 10^{-2}} = 1 + \alpha \quad \therefore \alpha = 0.267$$

Now

$$K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.01 \times 0.267 \times 0.267}{(1-0.267)} = 9.74 \times 10^{-4}$$

EXAMPLE 8.30

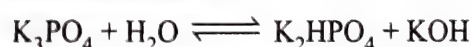
Calculate the pH of 0.1 M K_3PO_4 soln. The third dissociation constant of orthophosphoric acid is 1.3×10^{-12} . Assume that the hydrolysis proceeds only in the first step.

Sol. **First method:**

Use direct formula for the pH of salt of S_B/W_A

$$\begin{aligned} \text{pH} &= \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C) \\ &= \frac{1}{2} (14 + 11.86 - 1) = 12.43 \end{aligned}$$

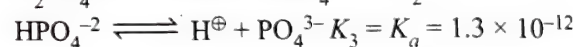
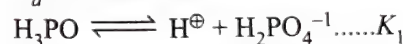
Second method:



Since hydrolysis proceeds only in 1 step.

$$\therefore [\text{OH}^{\ominus}] = C \cdot h = C \sqrt{\left(\frac{K_w}{K_a \cdot C}\right)} = \sqrt{\left(\frac{K_w \cdot C}{K_a}\right)}$$

K_a is III dissociation constant of acid H_3PO_4



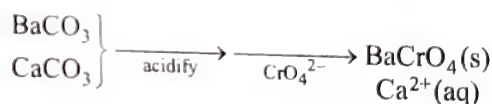
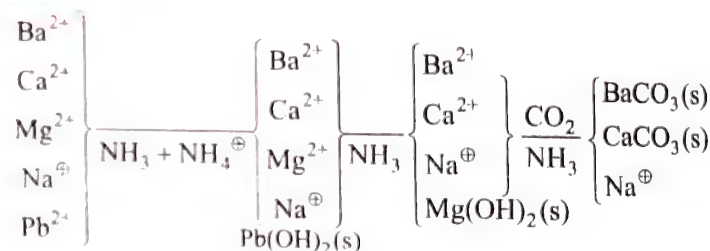
$$[\text{OH}^{\ominus}] = \left(\frac{10^{-14} \times 0.1}{1.3 \times 10^{-12}} \right)^{1/2} = 8.7 \times 10^{-2} \text{ M}$$

$$\therefore \text{pOH} = 1.5634; \text{pH} = 12.4366$$

EXAMPLE 8.31

Using CO_2 , NH_3 , NH_4NO_3 , and K_2CrO_4 as the only reagents, devise a qualitative analysis scheme for separating and identifying the following ions, which might all be present in the same mixture: Ba^{2+} , Ca^{2+} , Mg^{2+} , Na^{\oplus} , Pb^{2+} . Assume that each cation present is 0.10 M. State the conditions of pH and the reagent concentrations which are required in each step.

Sol.



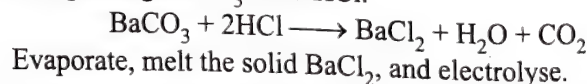
The Pb^{2+} ion is identified by acidification followed by treatment with chromate ion, upon which it forms a yellow solid precipitate. The Na^{\oplus} is identified by the intense yellow flame it yields.

EXAMPLE 8.32

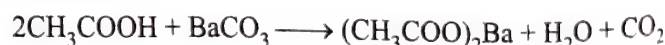
Assuming that the only source of periodic group IIA metals is an equimolar mixture of NaCl , BaCl_2 and MgCl_2 , suggest ways of preparing pure samples of

- a. MgSO_4 b. Ba Metal c. $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$

Sol. One possible method is given for each part (a) Add NaOH , precipitating $\text{Mg}(\text{OH})_2$. The Na^{\oplus} and Ba^{2+} remain in solution. After filtering the $\text{Mg}(\text{OH})_2$, add H_2SO_4 to it, yielding MgSO_4 in solution. Evaporate most of the water, causing MgSO_4 to crystallise.
(b) Add Na_2CO_3 to the solution, remaining from part (a), precipitating BaCO_3 . Add HCl .

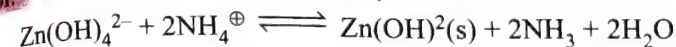


(c) To BaCO_3 obtained in part (b), add $\text{HC}_2\text{H}_3\text{O}_2$, and evaporate.



EXAMPLE 8.33

When a solution of Zn^{2+} was added to a solution of NaOH , a clear solution was obtained. When NH_4Cl was added to the clear solution, $\text{Zn}(\text{OH})_2$ precipitated. Using balanced chemical equations, explain these observations.



The acid NH_4^+ reacts with $\text{Zn}(\text{OH})_4^{2-}$ to cause $\text{Zn}(\text{OH})_2$ to precipitate.

EXAMPLE 8.34

Given reagents NH_3 , NaOH , HCl , and H_2S which one could be used to separate the ions in each of the following mixtures?

a. Cu^{2+} and Zn^{2+} b. Cu^{2+} and Al^{3+} c. Zn^{2+} and Al^{3+}

Sol.

NaOH in excess [precipitates $\text{Cu}(\text{OH})_2$ but forms soluble $\text{Zn}(\text{OH})_4^{2-}$] or H_2S in HCl (precipitates CuS but not ZnS)

NH_3 [forming $\text{Al}(\text{OH})_3(\text{s})$ and $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$], NaOH excess [forms $\text{Al}(\text{OH})_4^-(\text{aq})$ and $\text{Cu}(\text{OH})_2(\text{s})$, or $\text{H}_2\text{S} + \text{HCl}$ [forms CuS but does not react with Al^{3+}]

NH_3 [forms $\text{Al}(\text{OH})_3(\text{s})$ and $\text{Zn}(\text{NH}_3)_4^{2+}(\text{aq})$]

EXAMPLE 8.35

Estimate the K_{sp} of AgBr . Given $\Delta_f H^\ominus$ of Ag^\oplus , Br^\ominus , and AgBr are 25.31, -28.9, and -23.8 kcal; ΔS^\ominus of Ag^\oplus , Br^\ominus , and AgBr are 17.7, 19.3, and -25.6 cal/K.



To determine K_{sp} , one can calculate ΔG^\ominus from ΔH^\ominus and S^\ominus data.

$$\Delta H^\ominus = \Delta_f H^\ominus(\text{Ag}^\oplus) + \Delta_f H^\ominus(\text{Br}^\ominus) - \Delta_f H^\ominus(\text{AgBr})$$

$$= (25.31 \text{ kcal}) + (-28.9 \text{ kcal}) - (-23.8 \text{ kcal})$$

$$= 20.2 \text{ kcal}$$

$$\Delta S^\ominus = S^\ominus(\text{Ag}^\oplus) + S^\ominus(\text{Br}^\ominus) - S^\ominus(\text{AgBr})$$

$$= (17.7 \text{ cal K}^{-1}) + (19.3 \text{ cal K}^{-1}) - (25.6 \text{ cal K}^{-1})$$

$$= 11.4 \text{ cal K}^{-1}$$

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus = (20200 \text{ cal}) - (298 \text{ K})(11.4 \text{ cal K}^{-1})$$

$$= 16800 \text{ cal}$$

$$\Delta G^\ominus = (-2.30RT) (\log K_{\text{sp}})$$

$$\log K_{\text{sp}} = \frac{-\Delta G^\ominus}{2.30RT} = \frac{-16800 \text{ cal}}{(2.30)(1.99 \text{ cal K}^{-1})(298 \text{ K})} = 12.3$$

$$K = 4.8 \times 10^{-13}$$

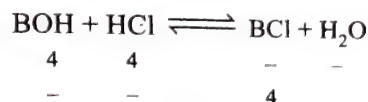
EXAMPLE 8.36

When 40 mL of a 0.1 M weak base, BOH is titrated with 0.10 M HCl , the pH of the solution at the end point is 5.5. What will be the pH if 10 mL of 0.10 M NaOH is added to the resulting solution?

Sol. At the end point, $\text{pH} = 5.5$ (i.e. an acidic solution).

It means salt formed at the end of neutralisation undergoes hydrolysis.

For 4 mmol (40×0.1), of weak base, 4 mmol of acid is required at the end point.



$$\Rightarrow \text{mmol of salt (BCl) formed} = 4$$

$$\Rightarrow [\text{BCl}] = 4/V \text{ where } V = V_{\text{HCl}} + V_{\text{base}}$$

$$\text{At the end point: } 4 = 0.10 \times V_{\text{HCl}}$$

$$\Rightarrow V_{\text{HCl}} = 40 \text{ mL}$$

$$\Rightarrow V = 40 + 40 = 80 \text{ mL}$$

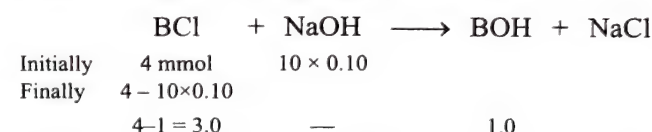
$$\Rightarrow [\text{BCl}] = 4/80 = 0.05 \text{ M}$$

Note that BCl is a salt of strong acid and weak base.

$$\Rightarrow [\text{H}^\oplus] = \sqrt{\frac{K_w C}{K_b}} \quad (\text{pH} = 5.5, \therefore [\text{H}^\oplus] = 3.2 \times 10^{-6} \text{ M})$$

$$\Rightarrow K_b = \frac{K_w C}{[\text{H}^\oplus]^2} = \frac{(10^{-14}) \times (0.05)}{(3.2 \times 10^{-6})^2} = 5.0 \times 10^{-5}$$

When 10 mL of 0.12 M NaOH is added:



It means a basic buffer containing 3.0 mmol of BCl and 1.0 mmol of BOH is formed. Find the pH by using Henderson's equation for basic buffer.

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]}$$

$$\Rightarrow \text{pOH} = -\log(5 \times 10^{-5}) + \log \frac{[3.0/V]}{[1.0/V]}$$

$$\Rightarrow \text{pOH} = 4.77$$

$$\Rightarrow \text{pH} = 14 - \text{pOH} = 9.22$$

EXAMPLE 8.37

What mass of Pb^{2+} ion is left in solution, when 50.0 mL of 0.20 M $\text{Pb}(\text{NO}_3)_2$ is added to 50.0 mL of 1.5 M NaCl ?

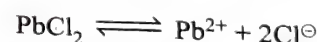
Sol. Assume complete precipitation of the Pb^{2+} followed by solution of the equilibrium concentration to be determined.

$$(50.0 \text{ mL})(0.20 \text{ M}) = 10 \text{ mmol } \text{Pb}^{2+}$$

$$(50.0 \text{ mL})(1.5 \text{ M}) = 75 \text{ mmol } \text{Cl}^\ominus$$



When lead ion concentration can exist in a solution of Cl^\ominus containing (75 mmol) - (20 mmol) = 55 mmol in 100 mL? $[\text{Cl}^\ominus] = 0.55 \text{ M}$



$$K_{\text{sp}} [\text{Pb}^{2+}] [\text{Cl}^\ominus]^2 = 1.7 \times 10^{-4}$$

$$[\text{Pb}^{2+}] = \frac{1.7 \times 10^{-4}}{(0.55)^2} = 5.6 \times 10^{-4} \text{ M}$$

$$(5.6 \times 10^{-4} \text{ mol L}^{-1})(0.100 \text{ L})(208 \text{ g mol}^{-1}) = 12 \text{ mg}$$

Single Correct Answer Type

- 100 mL of a buffer solution contains 0.1 M each of weak acid HA and salt NaA. How many gram of NaOH should be added to the buffer so that its pH will be 6? (K_a of HA = 10^{-5}).
(1) 0.328 (2) 0.458 (3) 4.19 (4) None
- K_a for the reaction:
 $\text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Fe}(\text{OH})^{2+}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
is 6.5×10^{-3} , what is the maximum pH value which could be used so that at least 80% of the total iron (III) in a dilute solution exists as Fe^{3+} ?
(1) 2.0 (2) ~ 2.4 (3) ~ 2.8 (4) ~ 1.6
- The $\text{p}K_b$ of CN^- is 4.7. The pH of solution prepared by mixing 2.5 mol of KCN of 2.5 mol of HCN in water and making the total volume upto 500 mL is
(1) 10.3 (2) 9.3 (3) 8.3 (4) 4.7
- A 0.1 molar solution of weak base BOH is 1% dissociated. If 0.2 mol of BCl is added in 1 L solution of BOH. The degree of dissociation of BOH will become
(1) 0.02 (2) 0.005 (3) 5×10^{-5} (4) 2×10^{-3}
- If the equilibrium constant of $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$ at 25°C is 2.5×10^{-6} , then equilibrium constant for $\text{BOH} + \text{H}^+ \rightleftharpoons \text{B}^+ + \text{H}_2\text{O}$ at the same temperature is
(1) 4.0×10^{-9} (2) 4.0×10^5
(3) 2.5×10^8 (4) 2.5×10^{-6}
- An aqueous solution of metal chloride MCl_2 (0.05 M) is saturated with H_2S (0.1 M). The minimum pH at which metal sulphide will be precipitated is
 $[K_{sp} \text{ MS} = 5 \times 10^{-21}, K_1(\text{H}_2\text{S}) = 10^{-7}, K_2(\text{H}_2\text{S}) = 10^{-14}]$
(1) 3.25 (2) 2.50 (3) 1.50 (4) 1.25
- The pH of a solution of weak base at neutralisation with strong acid is 8. K_b for the base is
(1) 1.0×10^{-4} (2) 1.0×10^{-6}
(3) 1.0×10^{-8} (4) None of these
- The ionisation constant of an acid base indicator (a weak acid) is 1.0×10^{-6} . The ionised form of the indicator is red and unionised form is blue. The pH change required to alter the colour of indicator from 80% red is
(1) 0.80 (2) 1.20 (3) 1.40 (4) 2.00
- K_{sp} of $\text{Mg}(\text{OH})_2$ is 4.0×10^{-6} . At what minimum pH, Mg^{2+} ions starts precipitating 0.01 M MgCl
(1) $2 + \log 2$ (2) $2 - \log 2$
(3) $12 + \log 2$ (4) $12 - \log 2$
- A solution of 0.1 M NaZ has pH = 8.90. The K_a of HZ is
(1) 6.3×10^{-11} (2) 6.3×10^{-10}
(3) 1.6×10^{-5} (4) 1.6×10^{-6}
- Phenolphthalein does not act as an indicator for the titration between
(1) HCl and NH_4OH (2) $\text{Ca}(\text{OH})_2$ and HCl
(3) NaOH and H_2SO_4 (4) KOH and CH_3COOH
- The pink colour of phenolphthalein in alkaline medium is due to
(1) OH^- ions (2) Positive ion
(3) Negative ion (4) Neutral form
- Methyl orange gives red colour in
(1) KOH solution (2) HCl solution
(3) Na_2CO_3 solution (4) NaCl solution
- A solution containing NH_4Cl and NH_4OH has $[\text{OH}^-] = 10^{-6} \text{ mol L}^{-1}$, which of the following hydroxides would be precipitated when this solution is added in equal volume to a solution containing 0.1 M of metal ions?
(1) $\text{Mg}(\text{OH})_2$, ($K_{sp} = 3 \times 10^{-11}$)
(2) $\text{Fe}(\text{OH})_2$ ($K_{sp} = 8 \times 10^{-16}$)
(3) $\text{Cd}(\text{OH})_2$ ($K_{sp} = 8 \times 10^{-6}$)
(4) AgOH ($K_{sp} = 5 \times 10^{-3}$)
- If equal volumes of BaCl_2 and NaF solutions are mixed, which of these combination will **not** give a precipitate? (K_{sp} of $\text{BaF}_2 = 1.7 \times 10^{-7}$).
(1) 10^{-3} M BaCl_2 and $2 \times 10^{-2} \text{ M NaF}$
(2) 10^{-3} M BaCl_2 and $1.5 \times 10^{-2} \text{ M NaF}$
(3) $1.5 \times 10^{-2} \text{ M BaCl}_2$ and 10^{-2} M NaF
(4) $2 \times 10^{-2} \text{ M BaCl}_2$ and $2 \times 10^{-2} \text{ M NaF}$
- The solubility of solid silver chromate, Ag_2CrO_4 , is determined in three solvents K_{sp} of $\text{Ag}_2\text{CrO}_4 = 9 \times 10^{-12}$
I. pure water II. 0.1 M AgNO_3
III. 0.1 M Na_2CrO_4
Predict the relative solubility of Ag_2CrO_4 in the three solvents.
(1) I = II = III (2) I < II < III
(3) II = III < I (4) II < III < I
- The solubility products of $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ are $\sqrt[3]{8.5 \times 10^{-23}}$ and 1.8×10^{-14} , respectively. If NH_4OH is added to a solution containing Al^{3+} and Zn^{2+} ions, then substance precipitated first is
(1) $\text{Al}(\text{OH})_3$ (2) $\text{Zn}(\text{OH})_2$
(3) Both (1) and (2) (4) None of these
- If $K_{sp}(\text{PbSO}_4) = 1.8 \times 10^{-8}$ and $K_a(\text{HSO}_4^-) = 1.0 \times 10^{-2}$ the equilibrium constant for the reaction.
 $\text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HSO}_4^-(\text{aq}) + \text{Pb}^{2+}(\text{aq})$ is
(1) 1.8×10^{-6} (2) 1.8×10^{-10}
(3) 2.8×10^{-10} (4) 1.0×10^{-2}
- Which one of the following is true for any diprotic acid, H_2X ?
(1) $K_{a2} > K_{a1}$ (2) $K_{a1} > K_{a2}$
(3) $K_{a2} = \frac{1}{K_{a1}}$ (4) $K_{a2} = K_{a1}$

20. K_{sp} of $Mg(OH)_2$ is 1×10^{-12} , 0.01 M $MgCl_2$ will be precipitating at the limiting pH:

- (1) 8 (2) 9 (3) 10 (4) 12

21. The solubility products of MA, MB, MC, and MD are 1.8×10^{-10} , 4×10^{-3} , 4×10^{-8} and 6×10^{-5} respectively. If a 0.01 M solution of MX is added dropwise to a mixture containing A^{\ominus} , B^{\ominus} , C^{\ominus} , and D^{\ominus} ions, then the one to be precipitated first will be

- (1) MA (2) MB (3) MC (4) MD

22. A solution is saturated with respect to $SrCO_3$ and SrF_2 . The $[CO_3^{2-}]$ was found to be 1.2×10^{-3} M. The concentration of F^{\ominus} in the solution would be

Given K_{sp} of $SrCO_3 = 7.0 \times 10^{-10} M^2$,

K_{sp} of $SrF_2 = 7.9 \times 10^{-10} M^3$,

- (1) 1.3×10^{-3} M (2) 2.6×10^{-2} M
(3) 3.7×10^{-2} M (4) 5.8×10^{-7} M

23. The number of S^{2-} ions present in 1 L of 0.1 M H_2S [$K_{a(H_2S)} = 10^{-21}$] solution having $[H^{\oplus}] = 0.1$ M is:

- (1) 6.023×10^3 (2) 6.023×10^4
(3) 6.023×10^5 (4) 6.023×10^6

24. The solubility of AgI in NaI solutions is less than that in pure water because:

- (1) AgI forms complex with NaI
(2) Of common ion effect
(3) Solubility product of AgI is less than that of NaI.
(4) The temperature of the solution decreases.

25. Three sparingly soluble salts M_2X , MX , and MX_3 have the same solubility product. Their solubilities will be in the order

- (1) $MX_3 > MX > M_2X$ (2) $MX_3 > M_2X > MX$
(3) $MX > MX_3 > M_2X$ (4) $MX > M_2X > MX_3$

26. When 0.2 M solution of acetic acid is neutralised with 0.2 M NaOH in 500 mL of water, the pH of the resulting solution will be: [pK_a of acetic acid = 4.74]

- (1) 12.67 (2) 7.87 (3) 8.87 (4) 7

27. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solutions of NaX is

- (1) 0.0001% (2) 0.01%
(3) 0.1% (4) 0.15%

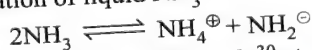
28. A certain buffer solution contains equal concentration of X^{\ominus} and HX. The K_b for X^{\ominus} is 10^{-10} . The pH of the buffer is

- (1) 4 (2) 7 (3) 10 (4) 14

29. A certain weak acid has a dissociation constant of 1.0×10^{-4} . The equilibrium constant for its reaction with a strong base is

- (1) 1.0×10^{-4} (2) 1.0×10^{-10}
(3) 1.0×10^{10} (4) 1.0×10^{14}

30. Auto-ionisation of liquid NH_3 is



with $K_{NH_3} = [NH_4^{\oplus}][NH_2^{\ominus}] = 10^{-30}$ at $-50^{\circ}C$

Number of amide ions (NH_2^{\ominus}), present per mm^3 of pure liquied NH_3 is

(1) 602 (2) 301 (3) 200 (4) 100
31. A mixture of weak acid is 0.1 M in $HCOOH$ ($K_a = 1.8 \times 10^{-4}$) and 0.1 M in $HOCN$ ($K_a = 3.1 \times 10^{-4}$). Hence, $[H_3O^{\oplus}]$ is

- (1) 7.0×10^{-3} M (2) 4.1×10^{-4} M
(3) 0.20 M (4) 4.1×10^{-3} M

32. pH of a solution made by mixing 50 mL of 0.2 M NH_4Cl and 75 mL of 0.1 M NaOH is [pK_b of $NH_3(aq) = 4.74$, $\log 3 = 0.47$]

- (1) 7.02 (2) 13.0 (3) 7.02 (4) 9.73

33. Some chemists at ISRO wished to prepare a saturated solution of a silver compound and they wanted it to have the highest concentration of silver ion possible. which of the following compounds would they use?

K_{sp} ($AgCl$) = 1.8×10^{-10} , K_{sp} ($AgBr$) = 5.0×10^{-13} ,

K_{sp} (Ag_2CrO_4) = 2.4×10^{-12} [Use $\sqrt[3]{0.6} = 0.84$]

- (1) $AgCl$ (2) $AgBr$ (3) Ag_2CrO_4 (4) all of these

34. An acid-base indicator has a $K_a = 3.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. Then

- (1) pH is 4.05 when indicator is 75% red.
(2) pH is 5.00 when indicator is 75% blue.
(3) Both (a) and (b) are correct.
(4) None of these.

35. The pH value of 0.001 M aqueous solution of NaCl is

- (1) 7 (2) 4
(3) 11 (4) Unpredictable

36. Which of the following will suppress the ionisation of acetic acid in aqueous solution?

- (1) NaCl (2) HCl
(3) KCl (4) Unpredictable

37. An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be

- (1) 9 (2) Between 6 and 7
(3) 7 (4) Unpredictable

38. Which of the following represents the conjugate pair of NH_3 ?

- (1) NH_2^{\ominus} (2) NH_4^{\oplus}
(3) Both (1) and (2) (4) N^{3-}

39. One of the following is a Bronsted acid but not a Bronsted base:

- (1) H_2S (2) H_2O (3) HCO_3^{\ominus} (4) NH_3

40. In the third group of qualitative analysis, the precipitating reagent is NH_4Cl/NH_4OH . The function of NH_4Cl is to

- (1) Increase the ionisation of NH_4OH .
(2) Suppress the ionisation of NH_4OH .
(3) Convert the ions of group third into their respective chlorides.
(4) Stabilise the hydroxides of group III cations.

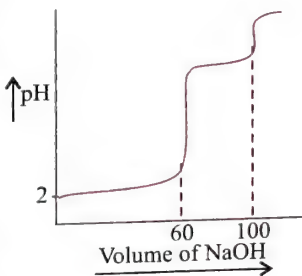
41. At a certain temperature the value of pK_w is 13.4 and the measured pH of soln is 7. The solution is

- (1) Acidic (2) Basic
(3) Neutral (4) Unpredictable

42. When 2 mol of HCl is added to 1 L of an acidic buffer, its pH changes from 3.4 to 2.9. The buffer capacity of the buffer solution is
(1) 2 (2) 0 (3) 4 (4) 8
43. Let the solubilities of AgCl in H_2O , and in 0.01 M CaCl_2 , 0.01 M NaCl, and 0.05 M AgNO_3 be S_1 , S_2 , S_3 , S_4 , respectively. What is the correct relationship between these quantities.
(1) $S_1 > S_2 > S_3 > S_4$ (2) $S_1 > S_2 = S_3 > S_4$
(3) $S_1 > S_3 > S_2 > S_4$ (4) $S_4 > S_2 > S_3 > S_1$
44. Which of the following salts will not undergo hydrolysis in water?
(1) Sodium sulphate (2) Ammonium sulphate
(3) Aluminium sulphate (4) All the salts will hydrolyse
45. Which of the following salts will not change the pH of pure water on dissociation?
(1) KCl (2) AlCl_3 (3) Na_2CO_3 (4) $\text{Al}_2(\text{SO}_4)_3$
46. A salt X is dissolved in water having pH = 7. The resulting solution has a pH more than 7. The salt is made by neutralisation of
(1) A strong acid and strong base
(2) A strong acid and strong weak base
(3) A weak acid and weak base
(4) A weak acid and strong base
47. The pH of a solution 7.00. To this solution, sufficient base is added to increase the pH to 12.0. The increase in OH^- ion concentration is
(1) 5 times (2) 1000 times
(3) 10^5 times (4) 4 times
48. Assuming H_2SO_4 to be completely ionised the pH of a 0.05 M aqueous solution of sulphuric acid is approximately
(1) 0.01 (2) 0.005 (3) 2 (4) 1
49. A solution has pOH equal to 13 at 298 K. The solution will be
(1) Highly acidic (2) Highly basic
(3) Moderately basic (4) Unpredictable
50. If ammonia is added to pure water, the concentration of a chemical species already present will decrease. The species is
(1) O_2^{\ominus} (2) OH^- (3) H_3O^+ (4) H_2O
51. The pH of a dilute solution of acetic acid was found to be 4.3. The addition of a small crystal of sodium acetate will cause pH to
(1) Become less than 4.3 (2) Become more than 4.3
(3) Remain equal to 4.3 (4) Unpredictable
52. Which of the following can act both as a Bronsted acid and a Bronsted base?
(1) O_2^{\ominus} (2) HCl (3) HSO_4^- (4) Na_2CO_3
53. Which of the following is a Lewis base?
(1) H_2O (2) Cl^- (3) BF_3 (4) NH_3
54. Which of the following is not a Lewis base?
(1) CN^- (2) ROH (3) NH_3 (4) AlCl_3
55. Conjugate base of OH^- is
(1) H_2O (2) H_3O^+ (3) H^+ (4) O^{2-}
56. Which of the following will have the largest pH?
(1) M/10 HCl (2) M/100 HCl
(3) M/10 NaOH (4) M/100 NaOH
57. Which one of following will have the largest pH?
(1) Solution containing 1×10^{-2} mol of $\text{K}_2\text{SO}_4 \text{ L}^{-1}$.
(2) Pure water.
(3) Solution containing 1.0×10^{-2} mol of HCl L^{-1} .
(4) Solution containing 1×10^{-2} mol of $\text{NH}_4\text{OH} \text{ L}^{-1}$.
58. When 20 mL of M/20 NaOH is added to 10 mL of M/10 HCl, the resulting solution will
(1) Turn blue litmus red.
(2) Turn phenolphthalein solution pink.
(3) Turns methyl orange red.
(4) Will have no effect on either red or blue litmus.
59. pOH of water is 7.0 at 298 K. If water is heated to 350 K, which of the following should be true?
(1) pOH will decrease
(2) pOH will increase
(3) pOH will remain seven
(4) Concentration of H^+ ions will increase but that of OH^- will decrease.
60. Solubility of salt A_2B_3 is 1×10^{-4} , its solubility product is
(1) 1.08×10^{20} (2) 1.08×10^{18}
(3) 2.6×10^{-18} (4) 1.08×10^{-18}
61. The value of K_{sp} is HgCl_2 at room temperature is 4.0×10^{-15} . The concentration of Cl^- ion in its aqueous solution at saturation point is
(1) 1×10^{-5} (2) 2×10^{-5} (3) 2×10^{-15} (4) 8×10^{-15}
62. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6.7} \text{ mol L}^{-1}$. What is the value of K_w at 90°C ?
(1) 10^{-6} (2) 10^{-12} (3) $10^{-13.4}$ (4) $10^{-6.7}$
63. What is the solubility of PbSO_4 in 0.01 M Na_2SO_4 solution if K_{sp} for $\text{PbSO}_4 = 1.25 \times 10^{-9}$?
(1) $1.25 \times 10^{-7} \text{ mol L}^{-1}$ (2) $1.25 \times 10^{-9} \text{ mol L}^{-1}$
(3) $1.25 \times 10^{-10} \text{ mol L}^{-1}$ (4) 0.10 mol L^{-1}
64. The pH of an aqueous solution of $\text{Ba}(\text{OH})_2$ is 10. If the K_{sp} of $\text{Ba}(\text{OH})_2$ is 1×10^{-9} , then the concentration of Ba^{2+} ions in the solution in mol L^{-1} is
(1) 1×10^{-2} (2) 1×10^{-4} (3) 1×10^{-1} (4) 1×10^{-5}
65. How many grams of NaOH must be dissolved in 1 L of the solution to give it a pH value of 12?
(1) 0.20 g L^{-1} (2) 0.40 g L^{-1}
(3) 0.10 g L^{-1} (4) 1.2 g L^{-1}
66. Which of the following solutions will have pH = 10 at 298 K?
(1) $1 \times 10^{-10} \text{ M}$ HCl solution
(2) $1 \times 10^{-4} \text{ M}$ NaOH solution
(3) $1 \times 10^{-10} \text{ M}$ NaOH solution
(4) Both (1) and (2)
67. An acid HA is 40% dissociated in an aqueous solution. The hydronium ion concentration of its 0.2 M solution would be
(1) 0.08 M (2) 0.4 M (3) 0.2 M (4) None

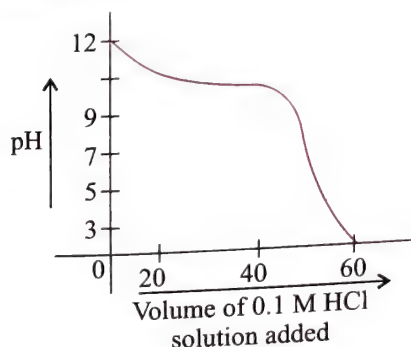
68. 20 cm^3 of $x \text{ M}$ solution of HCl is exactly neutralised by 40 cm^3 of 0.05 M NaOH solution, the pH of HCl solution is
 (1) 1.0 (2) 2 (3) 1.5 (4) 2.5
69. A monoprotic acid (HA) is 1% ionised in its aqueous solution of 0.1 M strength. Its pOH will be
 (1) 11 (2) 3 (3) 10 (4) 2
70. The pH of a solution is 5.00. To this solution, sufficient acid is added to lower the pH to 2.00. The corresponding increase in H_3O^+ ion concentration is
 (1) 1000 times (2) 2.5 times
 (3) 100 times (4) 5 times
71. What would be the solubility of silver chloride in 0.10 M NaCl solution?
 K_{sp} for $\text{AgCl} = 1.20 \times 10^{-10}$
 (1) 0.1 M (2) $1.2 \times 10^{-6} \text{ M}$
 (3) $1.2 \times 10^{-9} \text{ M}$ (4) $1.2 \times 10^{-10} \text{ M}$
72. Which of the following metal sulphides has maximum solubility in water?
 (1) CdS ($K_{\text{sp}} = 36 \times 10^{-30}$)
 (2) FeS ($K_{\text{sp}} = 11 \times 10^{-20}$)
 (3) HgS ($K_{\text{sp}} = 32 \times 10^{-54}$)
 (4) ZnS ($K_{\text{sp}} = 11 \times 10^{-22}$)
73. M_2SO_4 (M^+ is a monovalent metal ion) has a K_{sp} of 3.2×10^{-5} at 298 K . The maximum concentration of SO_4^{2-} ion that could be attained in a saturated solution of this solid at 298 K is
 (1) $3 \times 10^{-3} \text{ M}$ (2) $7 \times 10^{-2} \text{ M}$
 (3) $2.89 \times 10^{-4} \text{ M}$ (4) $2 \times 10^{-2} \text{ M}$
74. K_{sp} for lead iodate [$\text{Pb}(\text{IO}_3)_2$] is 3.2×10^{-14} at a given temperature. The solubility in mol L^{-1} will be
 (1) 2.0×10^{-5} (2) $(3.2 \times 10^{-7})^{1/2}$
 (3) (3.8×10^{-7}) (4) 4.0×10^{-6}
75. The pH of a 0.1 M solution of NH_4OH (having dissociation constant $K_b = 1.0 \times 10^{-5}$) is equal to
 (1) 10 (2) 6 (3) 11 (4) 12
76. The best indicator for the detection of the end point in the titration of a weak acid and a strong base is
 (1) Methyl orange (pH range 3 to 4)
 (2) Methyl red (pH range 4 to 6)
 (3) Thymol blue (pH range 8 to 3)
 (4) Phenolphthalein (pH range 8 to 10)
77. When solid KCl is added to a saturated solution of AgCl in H_2O ,
 (1) Nothing happens.
 (2) Solubility of AgCl decreases.
 (3) Solubility of AgCl increases.
 (4) Solubility product of AgCl increases.
78. Two buffer solutions, A and B, each made with acetic acid and sodium acetate differ in their pH by one unit, A has salt : acid = $x : y$, B has salt : acid = $y : x$. If $x > y$, then the value of $x : y$ is
 (1) 10,000 (2) 3.17 (3) 6.61 (4) 2.10
79. CaCO_3 and BaCO_3 have solubility product values 1×10^{-8} and 5×10^{-9} , respectively. If water is shaken up with both solids till equilibrium is reached, the concentration of CO_3^{2-} ion is
 (1) 1.5×10^{-8} (2) 1.225×10^{-4}
 (3) 2.25×10^{-9} (4) None of these
80. The pH of an acid buffer can be raised by 2 units by
 (1) Increasing the concentration of both weak acid and salt by two moles
 (2) Increasing the concentration of both the acid and salt by 10 times.
 (3) Diluting the solution by 10 times.
 (4) Increasing the concentration of the salt by 10 times and decreasing concentration of the acid by 10 times.
81. Buffer solutions can be prepared from mixtures of
 (1) HCl and NaCl (2) NaH_2PO_4 and Na_2HPO_4
 (3) CH_3COOH and NaCl (4) NH_4OH and NH_3
82. 20 mL of $\text{M}/10$ CH_3COOH solution is titrated with $\text{M}/10$ NaOH solution. After addition of 16 mL solution of NaOH . What is the pH of the solution ($\text{p}K_a = 4.74$)
 (1) 5.05 (2) 4.15 (3) 4.75 (4) 5.35
83. The K_a values of CaCO_3 and CaC_2O_4 in water are 4.7×10^{-9} and 1.3×10^{-9} , respectively, at 25°C . If a mixture of two is washed with H_2O , what is Ca^{2+} ion concentration in water?
 (1) 7.746×10^{-5} (2) 5.831×10^{-5}
 (3) 6.856×10^{-5} (4) 3.606×10^{-5}
84. What are the units in which the solubility product of $\text{Ca}_3(\text{PO}_4)_2$ is expressed?
 (1) mol dm^{-3} (2) $\text{mol}^2 \text{dm}^{-6}$
 (3) $\text{mol}^3 \text{dm}^{-9}$ (4) $\text{mol}^5 \text{dm}^{-15}$
85. The pH of 10^{-5} M HCl solution if 1 mL of it is diluted to 1000 mL is:
 (1) 5 (2) 8 (3) 7.02 (4) 6.98
86. Which of the following when mixed, will give a solution with $\text{pH} > 7$.
 (1) 0.1 M HCl + 0.2 M NaCl
 (2) 100 mL of 0.2 M H_2SO_4 + 100 mL of 0.3 M NaOH
 (3) 100 mL of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ + 100 mL of 0.1 M KOH
 (4) 25 mL of 0.1 M HNO_3 + 25 mL of 0.1 M NH_3
87. A solution of CaF_2 is found to contain $4 \times 10^{-4} \text{ M}$ of F^- ions. K_{sp} of CaF_2 is
 (1) 3.2×10^{-11} (2) 0.8×10^{-11}
 (3) 6.4×10^{-11} (4) 32×10^{-11}
88. At what pH will a 10^{-3} M solution of indicator with $K_b = 10^{-10}$ changes colour?
 (1) 10 (2) 4.0 (3) 3 (4) 7
89. If the dissociation constant of NH_4OH is 1.8×10^{-5} , the concentration of OH^- ions, in mol L^{-1} of 0.1 M NH_4OH is
 (1) 1.8×10^{-6} (2) 1.34×10^{-3}
 (3) 4.20×10^{-2} (4) 5.0×10^{-2}
90. pH signifies:
 (1) Puissance de hydrogen
 (2) $-\log [\text{H}^+]$
 (3) $14 - \text{pOH}$ (4) All of these
91. A solution with $\text{pH} = 2$ is more acidic than one with $\text{pH} = 6$ by a factor of
 (1) 4 (2) 12 (3) 400 (4) 10^4

92. A definite volume of a N/20 CH_3COOH ($pK_a = 4.7447$) is titrated with a strong base (NaOH). It is found that 80 equal sized drops of NaOH, added from a burette effects the complete neutralisation. Find the pH, when the acid soln is neutralised to the extent of 20%.
 (1) 4.14 (2) 9.86 (3) 5.34 (4) 8.68
93. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the same intestine is about 8. Aspirin will be
 (1) Unionised in the small intestine and in the stomach.
 (2) Completely ionised in the small intestine and in the stomach.
 (3) Ionised in the stomach and almost unionised in the small intestine.
 (4) Ionised in small intestine and almost unionised in the stomach.
94. Which of the following salt is basic?
 (1) HOCl (2) NaOCl (3) NaHSO_4 (4) NH_4NO_3
95. For the indicator the ratio $\frac{[\text{Ind}^\ominus]}{[\text{HIn}]}$ is 7.0 at pH of 4.3. K_a for the indicator is
 (1) 3.5×10^{-4} (2) 3.5×10^{-5}
 (3) 3.5×10^{-2} (4) 3.5×10^{-3}
96. When 0.002 mol of acid is added to 250 mL of a buffer solution, pH decreases by 0.02 units. The buffer capacity of the system is
 (1) 0.1 (2) 0.2 (3) 0.3 (4) 0.4
97. pH of an aqueous solution of 0.6 M NH_3 and 0.4 M NH_4Cl is 9.4 ($pK_b = 4.74$). The new pH when 0.1 M $\text{Ca}(\text{OH})_2$ solution is added to it
 (1) 9.86 (2) 9.53 (3) 9.7 (4) 9.4
98. Which of the following salts undergoes anionic hydrolysis?
 (1) CuSO_4 (2) NH_4Cl (3) FeCl_3 (4) Na_2CO_3
99. A saturated solution of Ag_2SO_4 is 2.5×10^{-2} M. The value of its solubility product is
 (1) 62.5×10^{-6} (2) 6.25×10^{-4}
 (3) 15.625×10^{-10} (4) 3.125×10^{-6}
100. Which one of the following is acid salt?
 (1) Na_2S (2) Na_2SO_3 (3) NaHSO_3 (4) Na_2SO_4
101. Which one is not an acid salt?
 (1) NaH_2PO_4 (2) NaH_2PO_2
 (3) NaH_2PO_3 (4) All of the above are acid salts
102. Which one of the following salts when dissolves in water hydrolyse?
 (1) NaCl (2) NH_4Cl (3) KCl (4) Na_2SO_4
103. Which of the following salt undergoes hydrolysis?
 (1) CH_3COOK (2) NaNO_3
 (3) KCl (4) K_2SO_4
104. Out of the following, the compound whose water solution has the highest pH is
 (1) NaCl (2) Na_2CO_3 (3) NH_4Cl (4) NaHCO_3
105. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with
 (1) 10^{-4} M (Ag^\oplus) and 10^{-4} M (Cl^\ominus)
 (2) 10^{-5} M (Ag^\oplus) and 10^{-5} M (Cl^\ominus)
 (3) 10^{-5} M (Ag^\oplus) and 10^{-6} M (Cl^\ominus)
 (4) 10^{-4} M (Ag^\oplus) and 10^{-10} M (Cl^\ominus)
106. The gastric juice in our stomach contains enough HCl to make the hydrogen ion concentration about 0.01 mol L^{-1} . The pH of gastric juice is
 (1) 0.01 (2) 1 (3) 2 (4) 14
107. Of the given anions, the strongest Bronsted base is
 (1) ClO^\ominus (2) ClO_2^\ominus (3) ClO_3^\ominus (4) ClO_4^\ominus
108. In decinormal solution, CH_3COOH acid is ionised to the extent of 1.3%. If $\log 1.3 = 0.11$, what is the pH of the solution?
 (1) 3.89 (2) 2.89
 (3) 4.89 (4) Unpredictable
109. An aqueous solution of aluminium sulphate would show
 (1) Acidic
 (2) Neutral
 (3) Basic
 (4) Both acidic and basic reaction.
110. The aqueous solution of AlCl_3 is acidic due to
 (1) Cation hydrolysis
 (2) Anion hydrolysis
 (3) Hydrolysis of both anion and cation
 (4) Dissociation
111. A solution contains 10 mL of 0.1 N NaOH and 10 mL of 0.05 Na_2SO_4 . pH of this solution is
 (1) 7 (2) Less than 7
 (3) Greater than 7 (4) Zero
112. 20 mL of 0.1 N HCl is mixed with 20 mL of 0.1 N KOH . The pH of the solution would be
 (1) 0 (2) 7 (3) 2 (4) 9
113. 0.1 M solution of which of the substances will behave basic?
 (1) Sodium borate (2) Ammonium ditioride
 (3) Calcium nitrate (4) Sodium sulphate
114. In which of the following solvents will AgBr has highest solubility?
 (1) 10^{-3} M NaBr (2) 10^{-3} M NH_4OH
 (3) Pure water (4) 10^{-3} M HBr
115. Which of the following mixture solution has $\text{pH} \approx 1.0$?
 (1) 100 mL M/10 HCl + 100 mL M/10 NaOH
 (2) 55 mL M/10 HCl + 45 mL M/10 NaOH
 (3) 10 mL M/10 HCl + 90 mL M/10 NaOH
 (4) 75 mL M/5 HCl + 25 mL M/5 NaOH
116. Fear or excitement, generally cause on to breathe rapidly and it results in the decrease of CO_2 concentration in blood. In what way will it change the pH of blood?
 (1) pH will increase (2) pH will decrease
 (3) No change (4) pH will adjust to 7

117. Which buffer solution out of the following will have $\text{pH} > 7$?
- $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 - $\text{HCOOH} + \text{HCOOK}$
 - $\text{CH}_3\text{COONH}_4$
 - $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
118. Which of the following is most soluble?
- Bi_2S_3 ($K_{\text{sp}} = 1 \times 10^{-70}$)
 - MnS ($K_{\text{sp}} = 7 \times 10^{-16}$)
 - CuS ($K_{\text{sp}} = 8 \times 10^{-37}$)
 - Ag_2S ($K_{\text{sp}} = 6 \times 10^{-51}$)
119. If H^+ ion concentration of a solution is increased by 10 times, its pH will
- Increase by 1
 - Remains unchanged
 - Decreases by 1
 - Increase by 10
120. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is
- 1.74×10^{-5}
 - 3.52×10^{-3}
 - 6.75×10^{-4}
 - 5.38×10^{-2}
121. The following graph represents the titration of pH vs volume
- 
- A diprotic acid.
 - Two monoprotic acids with the same K_a but different concentrations.
 - Two monoprotic acids with different K_a but the same concentration.
 - Two monoprotic acids with different K_a and different concentrations.

Multiple Correct Answers Type

- 0.1 mol of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol of HCl and diluted to 1 L. Which statement is correct?
 - The concentration of H^+ ion is 8×10^{-11} M.
 - The concentration of H^+ ion is 8×10^{-5} M.
 - The pH of solution is 9.8
 - The pOH of solution is 10.2.
- When weak base solution (50 mL of 0.1 N NH_4OH) is titrated with strong acid (0.1 N HCl), the pH of the solution initially decreases fast and then decreases slowly till near the equivalence point (as shown in figure). Which of the following is/are correct.



- The slow decrease of pH is due to the formation of an acidic buffer solution after the addition of some HCl.
 - The slope of shown graph will be minimum when 25 mL of 0.1 N HCl is added.
 - The slow decrease of pH is due to the formation of basic buffer solution.
 - The initial fast decrease in pH is due to fast consumption of OH^- ions by HCl.
3. Which of the following statements about a weak acid strong base titration is/are correct?
- The pH after the equivalence point of the weak acid strong base titration is determined by using the K_b expression for the conjugate base.
 - A buffer solution of weak acid and its conjugate base is formed before the equivalence is reached.
 - The pH at the equivalence point of a weak monoprotic acid strong base titration is equal to the pH at the equivalence point of a strong acid-strong base titration.
 - The increase in pH in the region near the equivalence point of a weak acid strong base titration is greater than the pH change in the same region of a strong acid strong base titration.
4. An acid-base indicator has $K_a = 10^{-5}$. The acid form of the indicator is red and basic form is blue. Which of the following is/are correct?
- At pH = 4.52, solution is red
 - At pH = 5.47, solution is blue.
 - At pH = 6, solution is 75% red
 - At pH = 8, solution is 75% blue.
5. When HCl is passed through a saturated solution of common salt, pure NaCl is precipitated because:
- HCl is highly soluble in water.
 - The ionic product $[\text{Na}^+][\text{Cl}^-]$ exceeds its solubility product (K_{sp}).
 - The K_{sp} of NaCl is lowered by the presence of Cl^- ions.
 - HCl causes precipitation.
6. Excess of $\text{Ag}_2\text{SO}_4(\text{s})$, $\text{BaSO}_4(\text{s})$, and $\text{Ba}_3(\text{PO}_4)_2(\text{s})$ are simultaneously in equilibrium with distilled water. Which of the following is (are) true? Assume no hydrolysis of dissolved ions.
- $[\text{Ag}^+] + 2[\text{Ba}^{2+}] = 2[\text{SO}_4^{2-}] + 3[\text{PO}_4^{3-}]$
 - $2[\text{Ag}^+] + 4[\text{Ba}^{2+}] = 2[\text{SO}_4^{2-}] + 2[\text{PO}_4^{3-}]$
 - $2[\text{Ag}^+] + 3[\text{Ba}^{2+}] = 2[\text{SO}_4^{2-}] + 2[\text{PO}_4^{3-}]$
 - $[\text{Ag}^+] + [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] + [\text{PO}_4^{3-}]$
7. A solution is found to contain $[\text{Cl}^-] = 1.5 \times 10^{-1}$ M; $[\text{Br}^-] = 5.0 \times 10^{-4}$ M; $[\text{CrO}_4^{2-}] = 1.9 \times 10^{-2}$ M. A solution of AgNO_3 (100% dissociated) is added to the above solution drop by drop. Which silver salt will precipitate first?
- Given: $K_{\text{sp}}(\text{AgCl}) = 1.5 \times 10^{-10}$, $K_{\text{sp}}(\text{AgBr}) = 5.0 \times 10^{-13}$, $K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = 1.9 \times 10^{-12}$.

- (1) AgCl (2) AgBr
(3) Ag₂CrO₄ (4) AgCl and AgBr together
8. Hg₂CrO₄ just begins to precipitate when equal volumes of 4×10^{-4} M Hg₂(NO₃)₂ and 2×10^{-5} M K₂CrO₄ are combined. What is the approximate K_{sp} value of Hg₂CrO₄?
(1) 1×10^{-18} mol L⁻¹ (2) 8×10^{-9} mol L⁻¹
(3) 2×10^{-9} mol L⁻¹ (4) 4×10^{-9} mol L⁻¹
9. What is general criteria of choosing a suitable indicator for a given titration?
(1) The indicator should have a broad pH range.
(2) pH at the end point of titration should be close to neutral point of indicator
(3) The indicator should have neutral point at pH = 7.
(4) The indicator must show a sharp colour change near the equivalence point of titration point.
10. Which of the following are true for an acid-base titration?
(1) Indicators catalyse the acid-base reactions by releasing or accepting H⁺ ions.
(2) Indicators do not significantly affect the pH of the solution to which they are added
(3) Acid-base reactions do not occur in the absence of indicators
(4) Indicators have different colours in dissociated and undissociated forms.
11. An acid-base indicator has $K_a = 3.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. Then:
(1) pH is 4.04 when indicator is 75% red.
(2) pH is 5.00 when indicator is 75% blue.
(3) pH is 5.00 when indicator is 75% red.
(4) pH is 4.05 when indicator is 75% blue.
12. At the end point, there is a sharp change of colour in the indicator. This happens because the
(1) pH at end point changes sharply.
(2) Structure of the indicator changes.
(3) Colour of indicator is adsorbed by water.
(4) Dissociation constant of acids and base differ by 10.
13. For a series of indicators, the colours and pH range over which colour change takes place are as follows:

Indicator	Colour change over pH range
U	Yellow to blue pH 0.0 to 1.6
V	Red to yellow pH 2.8 to 4.1
W	Red to yellow pH 4.2 to 5.8
X	Yellow to blue pH 6.0 to 7.7
Y	Colourless to red pH 8.2 to 10.0

Which of the following statements is correct?

- (1) Indicator V could be used to find the equivalence point for 0.01 M acetic acid and 0.1 M ammonium hydroxide (ammonia solution) titration.

- (2) Indicator Y could be used to distinguish between 0.1 M HCl and 0.001 M NaOH solutions in water.
(3) Indicator X could be used to distinguish between solution of ammonium chloride and sodium acetate.
(4) Indicator W could be suitable for use in determining the concentration of acetic acid in vinegar by base titration.
14. $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$; K_{a1} :
 $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$; K_{a2} :
 $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$; K_{a3} :
Mark out the incorrect statements:
(1) $K_{a1} > K_{a2} > K_{a3}$
(2) $\text{pH}(\text{H}_2\text{PO}_4^-) = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$
(3) Both H_3PO_4 and H_2PO_4^- are more acidic than HPO_4^{2-}
(4) Only HPO_4^{2-} is amphiprotic anion in the solution.
15. Aqueous solutions of HNO₃, CH₃COOH, and CH₃COOK of identical concentrations are given. The pair(s) of the solution which may form a buffer upon mixing is(are):
(1) NaOH and CH₃COOH
(2) HNO₃ and CH₃COOK
(3) CH₃COOH and CH₃COOK
(4) HNO₃ + CH₃COOH
16. To which of the solution, addition of water would not effect the pH?
(1) 100 mL of 0.2 M CH₃COOH + 100 mL of 0.1 M NaOH
(2) 100 mL of 0.2 M CH₃COOH + 100 mL of 0.2 M NaOH
(3) 200 mL of 0.2 M CH₃COOH + 100 mL of 0.1 M NaOH
(4) 100 mL of 0.2 M CH₃COOH + 200 mL of 0.2 M NaOH
17. Which of the following salt solutions has pH < 7?
(1) NH₄F (2) Cr(NO₃)₃
(3) [(CH₃)₃NH⁺]Cl⁻ (4) CaI₂
18. Which of the following represents hydrolysis?
(1) $\text{NH}_4^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}_3\text{O}^+$
(2) $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
(3) $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$
(4) $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$
19. The pH values of aqueous solutions of which of the following compounds does not change on dilution?
(1) PhCOONH₄ (2) NH₄CN
(3) HCOONa (4) NH₄Cl
20. In H₃PO₄ which of the following is true?
(1) $K_a = K_{a1} \times K_{a2} \times K_{a3}$ (2) $K_{a1} < K_{a2} < K_{a3}$
(3) $K_{a1} > K_{a2} > K_{a3}$ (4) $K_{a1} = K_{a2} = K_{a3}$
21. The degree of hydrolysis for a salt of strong acid and weak base
(1) Is independent of dilution
(2) Increases with dilution
(3) Increases with decrease in K_b of the bases
(4) Decreases with decrease in temperature

22. A solution containing a mixture of 0.05 M NaCl and 0.05 M NaI is taken. (K_{sp} of AgCl = 10^{-10} and K_{sp} of AgI = 4×10^{-16}). When AgNO₃ is added to such a solution:
- (1) The concentration of Ag⁺ required to precipitate Cl⁻ is 2×10^{-9} mol L⁻¹.
 - (2) The concentration of Ag⁺ required to precipitate I⁻ is 8×10^{-15} mol L⁻¹.
 - (3) AgCl and AgI will be precipitate together.
 - (4) First AgI will be precipitated.
23. Which of the following is (are) correct when 0.1 L of 0.0015 M MgCl₂ and 0.1 L of 0.025 M NaF are mixed together? (K_{sp} of MgF₂ = 3.7×10^{-8}).
- (1) MgF₂ remains in solution
 - (2) MgF₂ precipitates out
 - (3) MgCl₂ precipitates out
 - (4) Cl⁻ ions remain in solution
24. Choose the correct statement:
- (1) pH of acidic buffer solution decreases if more salt is added
 - (2) pH of acidic solution increases if more salt is added.
 - (3) pH of basic buffer decreases if more salt is added.
 - (4) pH of basic buffer increases if more salt is added.
25. Which of the following is(are) correct for buffer solution?
- (1) Acidic buffer will be effective within in the pH range ($pK_a \pm 1$).
 - (2) Basic buffer will be effective within the pH range ($pK_w - pK_b \pm 1$).
 - (3) H₃PO₄ + NaH₂PO₄ is not a buffer solution.
 - (4) Buffers behave most effectively when the [Salt]/[Acid] ratio equal to 1.
26. A solution is prepared by dissolving 1.5 g of a monoacidic base into 1.5 kg of water at 300 K, which showed a depression in freezing point by 0.165° C. When 0.496 g of the same base titrated, after dissolution, requires 40 mL of semimolar H₂SO₄ solution. If K_f of water is 1.86 K kg mol⁻¹, then select the correct statement(s) out of the following (assuming molarity = molality):
- (1) The pH of the solution of weak base is 12.9.
 - (2) The ionisation constant of the base is 8×10^{-3} .
 - (3) The osmotic pressure of the aqueous solution of base is 21.67 atm
 - (4) The base is 10% ionized in aqueous solution.
27. A solution of 0.01 M Fe²⁺ in a saturated H₂S solution and (i) 0.2 M of H⁺ (ii) 0.001 M of H⁺. ($K_1 \times K_2$ of H₂S = 10^{-21} , K_{sp} FeS = 3.7×10^{-19}).
- Which of the following statement is/are correct
- (1) FeS will precipitate in solution (i).
 - (2) FeS will not precipitate in solution (i).
 - (3) FeS will precipitate in solution (ii).
 - (4) FeS will not precipitate in solution (ii).
28. Which statements is/are correct?
- (1) 0.1 M NH₃ solution will precipitate Fe(OH)₂ from a 0.1 M solution Fe²⁺.
 - (2) 0.1 M NH₃ solution will not precipitate Mg(OH)₂ from a solution which is 0.2 M in \rightleftharpoons and 0.1 M in Mg²⁺
 - (3) 0.1 M NH₃ solution will not precipitate AgOH from a solution which is 0.01 M in Ag⁺.
 - (4) Will precipitate in part (3).
29. Which statements is/are correct?
- (1) Compared to a strong acid, a weak acid titration with base starts at a higher pH.
 - (2) Compared to a strong base, a weak base titration ends at a lower pH.
 - (3) In both (1) and (2) titration curve is shortened at each end.
 - (4) For titration of a weak acid and a weak base, the nearly vertical portion of the curve would be insufficient for an effective titration.
30. Which of the following solution will have pH = 13?
- (1) 2 g NaOH in 500 mL solution.
 - (2) 100 mL solution of 0.05 M Ca(OH)₂.
 - (3) 100 mL solution of 0.1 N Ca(OH)₂.
 - (4) 4 g NaOH in 500 mL solution.
31. Which of the following statements(s) is(are) correct?
- (1) The pH of 1.0×10^{-8} M solution of HCl is 8.
 - (2) The conjugate base of H₂PO₄⁻ is HPO₄²⁻.
 - (3) Autoprotolysis constant of water increases with temperature.
 - (4) When a solution of weak monoprotic acid is titrated against a strong base, at half-neutralisation, point pH = (1/2) pK_a.
32. The pH of 0.1 M solution of the following salts increases in the order
- (1) NaCl < NH₄Cl < NaCN < HCl
 - (2) HCl < NH₄Cl < NaCl < NaCN
 - (3) NaCN < NH₄Cl < NaCl < HCl
 - (4) HCl < NaCl < NaCN < NH₄Cl
33. A buffer solution can be prepared from a mixture of
- (1) Sodium acetate and acetic acid in water.
 - (2) Sodium acetate and hydrochloric acid in water.
 - (3) Ammonia and ammonium chloride in water.
 - (4) Ammonia and sodium hydroxide in water.

Linked Comprehension Type

Paragraph 1

Pb(IO₃)₂ is a sparingly soluble salt ($K_{sp} = 2.6 \times 10^{-13}$). To 35 mL of 0.15 M Pb(NO₃)₂ solution, 15 mL of 0.8 M KIO₃ solution is added, and a precipitate of Pb(IO₃)₂ is formed.

1. Which is the limiting reactant of the reaction that takes place in the solution?

(1) Pb(IO ₃) ₂	(2) Pb(NO ₃) ₂
(3) KIO ₃	(4) Both (2) and (3).
2. What will be the molarity of IO₃⁻ ions in the solution after completion of the reaction?

(1) 0.152	(2) 0.081
(3) 0.41	(4) 0.03

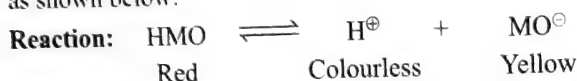
3. What will the molality of Pb^{2+} ions in the solution after completion of the reactions?

- (1) 8.4×10^{-10} (2) 1.6×10^{-10}
(3) 2.8×10^{-10} (4) 6.1×10^{-10}

Paragraph 2

Acid-base indicator such as methyl orange, phenolphthalein, and bromothymol blue are substances which change colour according to the hydrogen ion concentration of the solution to which they are added.

Most indicators are weak acids (or more rarely weak base) in which the undissociated and dissociated forms have different and distinct colours. If methyl orange is used as the example and the undissociated form is written as HMO, then dissociation occurs as shown below:



The indicator should have a sharp colour change with the equivalence point of the titration. Usually the colour change of the indicator occurs over a range of about two pH units. It should be noted that the eye cannot detect the exact end point of the titration. The $\text{p}K_a$ of the indicator should be near the pH of the solution at the equivalence point.

4. Which of the following situation exists at the equivalence point of a titration?

- (1) $[\text{H}^+] = 10^{-7} \text{ M}$ (2) $[\text{H}^+] = [\text{OH}^-]$
(3) $[\text{OH}^-] = 10^{-7} \text{ M}$ (4) $\frac{[\text{H}^+]}{[\text{OH}^-]} = 10^{-14}$

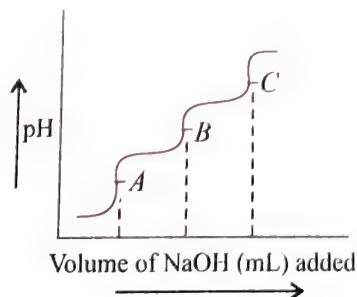
5. Given that the K_a (methyl orange) = 4.0×10^{-4} , a solution at pH = 2 containing the indicator would be

- (1) Orange (2) Yellow (3) Colourless (4) Red

Paragraph 3

Acidic solution is defined as a solution whose $[\text{H}^+] > [\text{OH}^-]$.

Base solution has $[\text{OH}^-] > [\text{H}^+]$. During acid-base titrations, pH of the mixture will change depending on the amount base added. This variation is shown in the form of graph by making plot between pH vs volume of base added. These graphs are known as titration curves 100 mL of 0.1 M H_3A ($K_{a1} = 10^{-3}$, $K_{a2} = 10^{-5}$, $K_{a3} = 10^{-7}$) is titrated against 0.1 M NaOH. The titration curve is as follows.



6. What is the pH at point A?

- (1) 3 (2) 4 (3) 5 (4) 6

7. What would be the pH if more of NaH_2A is added to the titration mixture at point C?

- (1) 11.0 (2) 10.2 (3) 9.7 (4) 7.7

8. What will be the change in pH from point B to point C?

- (1) 2.8 (2) 3.2 (3) 4.6 (4) 0.94

Paragraph 4

In qualitative analysis, cations of group II as well as group IV both are precipitated in the form of sulphides. Due to low value of K_{sp} of group II sulphides, group reagent is H_2S in the presence of dil. HCl, and due to high value of K_{sp} of group IV sulphides, group reagent is H_2S in the presence of NH_4OH and NH_4Cl .

In a solution containing 0.1 M each of Sn^{2+} , Cd^{2+} , and Ni^{2+} ions, H_2S gas is passed.

K_{sp} of $\text{SnS} = 8 \times 10^{-29}$, K_{sp} of $\text{CdS} = 1.5 \times 10^{-28}$, K_{sp} of $\text{NiS} = 3 \times 10^{-21}$, K_1 of $\text{H}_2\text{S} = 1 \times 10^{-7}$, K_2 of $\text{H}_2\text{S} = 1 \times 10^{-14}$

9. If H_2S is passed into the above mixture in the presence of HCl, which ion will be precipitated first?

- (1) SnS (2) CdS
(3) NiS (4) SnS and CdS (both together)

10. At what value of pH, NiS will start to precipitate?

- (1) 12.76 (2) 7 (3) 1.24 (4) 4

11. Which of the following sulphides is more soluble in pure water?

- (1) Cds (2) NiS
(3) SnS (4) Equal solubility for all

12. If 0.1 M HCl is mixed in the solution containing only 0.1 M Cd^{2+} ions and saturated with H_2S , then $[\text{Cd}^{2+}]$ remaining in the solution after CdS stops to precipitate is:

- (1) 10^{-8} (2) 8.2×10^{-9}
(3) 5.6×10^{-6} (4) 5.6×10^{-10}

Paragraph 5

The degree of dissociation of weak electrolyte is inversely proportional to the square root of concentration. It is called Ostwald's dilution law.

$\alpha = \sqrt{\frac{K_a}{c}}$. As the temperature increases, degree of dissociation will increase.

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} \text{ if concentration is same.}$$

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{c_2}{c_1}} \text{ if acid is same.}$$

13. 0.01 M CH_3COOOH has 4.24% degree of dissociation, the degree of dissociation of 0.1 M CH_3COOH will be

- (1) 1.33% (2) 4.24%
(3) 5.24% (4) 0.33%

14. pH of 0.005 M HCOOH [$K_a = 2 \times 10^{-4}$] is equal to

- (1) 3 (2) 2 (3) 4 (4) 5

15. a_1 and a_2 are in ratio of 1 : 2, $K_{a1} = 2 \times 10^{-4}$. What will be K_{a2} ?

- (1) 8×10^{-4} (2) 2×10^{-4}
(3) 4×10^{-4} (4) 1×10^{-4}

Paragraph 6

The following solutions are mixed: 500 mL of 0.01 M AgNO_3 and 500 mL solution that was both 0.01 M in NaCl and 0.01 M in NaBr . Given $K_{sp} \text{AgCl} = 10^{-10}$, $K_{sp} \text{AgBr} = 5 \times 10^{-13}$.

16. Calculate the $[\text{Cl}^\ominus]$ in the equilibrium solution.

- (1) $5 \times 10^{-5} \text{ M}$ (2) 2.5×10^{-5}
(3) $5 \times 10^{-3} \text{ M}$ (4) $2.5 \times 10^{-3} \text{ M}$

17. Calculate the $[\text{Ag}^\oplus]$ in the equilibrium solution.

- (1) $2.0 \times 10^{-8} \text{ M}$ (2) $2.0 \times 10^{-10} \text{ M}$
(3) $2.5 \times 10^{-5} \text{ M}$ (4) $2.5 \times 10^{-8} \text{ M}$

18. Calculate the $[\text{Br}^\ominus]$ in the equilibrium solution.

- (1) $2.0 \times 10^{-8} \text{ M}$ (2) $2.0 \times 10^{-10} \text{ M}$
(3) $2.5 \times 10^{-5} \text{ M}$ (4) $2.5 \times 10^{-8} \text{ M}$

Paragraph 7

When 1.5 mol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is dissolved in enough water to make 1.0 L of solution.

Given: $K_f \text{CuCl}^\oplus = 1.0$ (K_f is the formation constant of CuCl^\oplus)

19. $[\text{Cu}^{2+}]$ in solution is

- (1) 1.0 M (2) 0.5 M (3) 2.0 M (4) None

20. $[\text{Cl}^\ominus]$ in solution is

- (1) 2.0 M (2) 1.0 M (3) 3.0 M (4) None

21. $[\text{CuCl}^\oplus]$ in solution is

- (1) 1.0 M (2) 2.0 M (3) 3.0 M (4) 0.5 M

Paragraph 8

Acid rain takes place due to combination of acidic oxides with water and it is an environmental concern all over the world. Assuming rain water is uncontaminated with HNO_3 or H_2SO_4 and is in equilibrium with $1.25 \times 10^{-4} \text{ atm CO}_2$. The Henry's law constant (K_H) is $1.25 \times 10^6 \text{ torr}$. K_{a1} of $\text{H}_2\text{CO}_3 = 4.3 \times 10^{-7}$.

Given: $K_f \text{CuCl}^\oplus = 1.0$ (K_f is formation constant of CuCl^\oplus)

22. What is the pH of natural rain water?

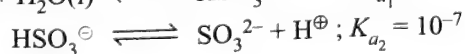
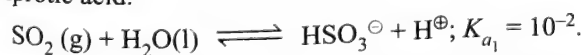
- (1) 5.64 (2) 7.00 (3) 5.87 (4) 7.40

23. If SO_2 content in the atmosphere is 0.64 ppm by volume, pH of rain water is (assume 100% ionisation of acid rain as monobasic acid).

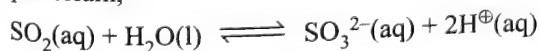
- (1) 4.0 (2) 5.0 (3) 6.0 (4) 7.0

Paragraph 9

In atmosphere, SO_2 and NO are oxidised to SO_3 and NO_2 , respectively, which react with water to give H_2SO_4 and HNO_3 . The resultant solution is called acid rain. SO_2 dissolves in water to form diprotic acid.



and for equilibrium,



$$K_a = K_{a1} \times K_{a2} = 10^{-9} \text{ at } 300\text{K}.$$

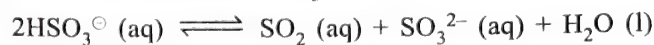
24. Which of the following reagents will give white precipitate with the aqueous solution of sulphurous acid?

- (1) BaCl_2 (2) HCl (3) NaCl (4) KCl

25. The pH of 0.01 M aqueous solution of sodium sulphite (Na_2SO_3)

- (1) 4.5 (2) 8.5 (3) 9.0 (4) 9.5

26. The dominant equilibrium in an aqueous solution of sodium hydrogen sulphite (NaHSO_3) is



The equilibrium constant for the above reaction is

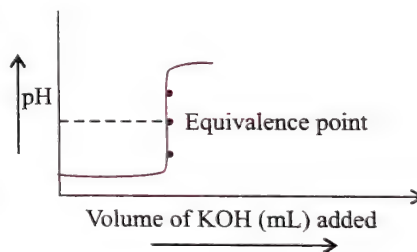
- (1) 10^{-3} (2) 10^{-5} (3) 10^{-6} (4) 10^{-9}

27. Which of the following statement is correct?

- (1) H_2SO_3 is less acidic than H_2SO_4 .
(2) HNO_3 is less acidic than HNO_2 .
(3) $\text{SO}_2(\text{g})$ is reduced in the atmosphere during thunderstorm.
(4) CO_2 gas develop more acidity in rain water than SO_2 .

Paragraph 10

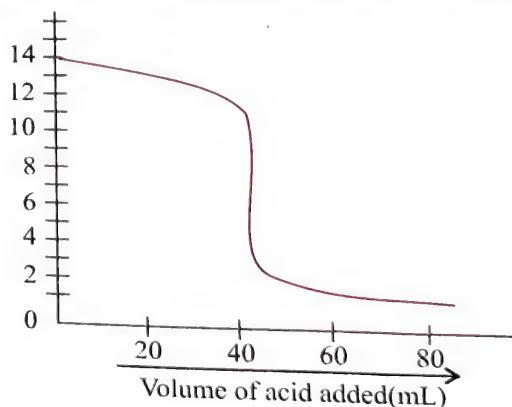
In acid-base titration react rapidly to neutralise each other. Equivalence point is a point at which the acid and the base (or oxidising agent and reducing agent) have been added in equivalent quantities. The end point is the point at which the titration stops. Since the purpose of the indicator is to stop the titration close to the point at which the acid and base were added in equivalent quantities, it is important that the equivalent point and the end point be as close as possible. The indicator must change colour at a pH close to that of a solution of the salt of the acid and base. Significantly, the pH changes most rapidly near the equivalence point. The exact shape of a titration curve depends on K_a and K_b of acid and base.



28. The following curve represents titration curve of HCl against KOH . The pH at equivalent point is

- (1) 3 (2) 6 (3) 7 (4) 8

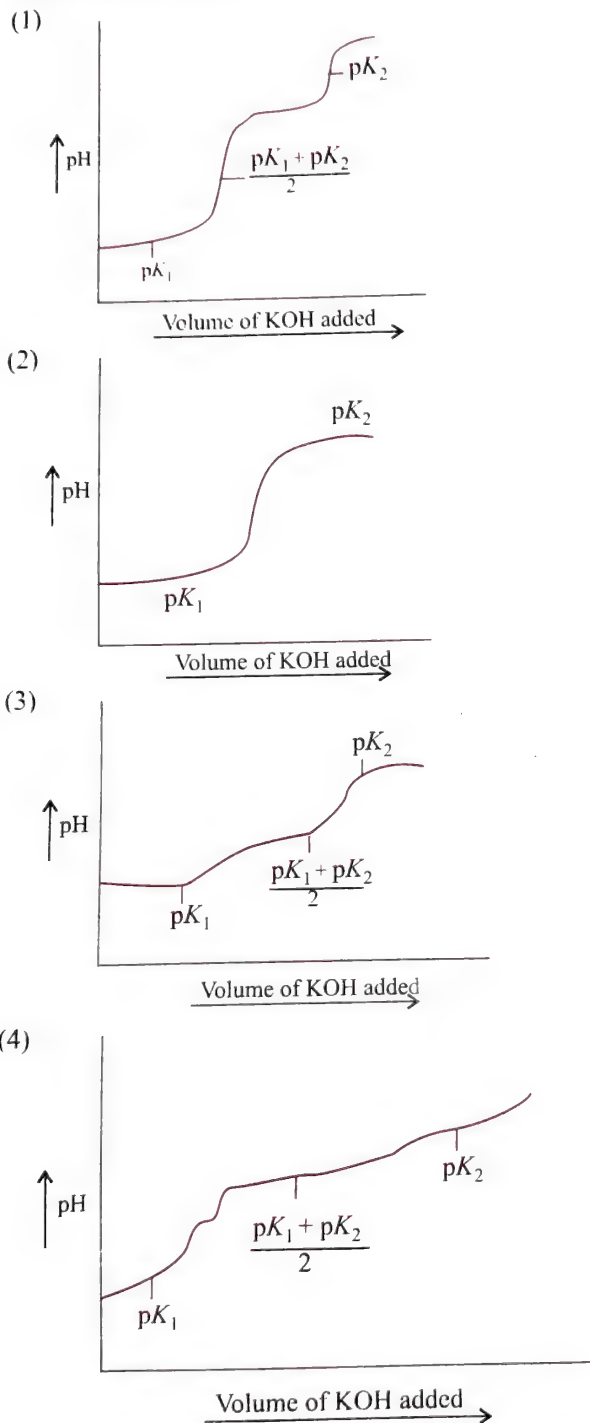
Examine the titration curve below and answer the question.



29. The curve represents the titration of

- (1) CsOH by HBr (2) HCl by NaOH
(3) HCl by KOH (4) NH_3 by HNO_3

30. The suitable indicator for the titration is
 (1) Methyl orange (2) Bromothymol
 (3) Methyl red (4) All of these
31. The pH at equivalence point is
 (1) 2 (2) 3 (3) 7 (4) 11
32. Which of the following curves indicates the titration of a weak diprotic acid by KOH of equivalent strength?

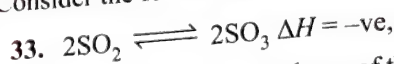


Paragraph 11

Physical and chemical equilibria can respond to a change in their pressure, temperature, and concentration of reactants and products. To describe the change in the equilibrium, we have a principle named Le Chatelier's principle. This we can define in terms of energy, as the free energy change in equilibrium is zero means the system is stable. So if we are doing some changes in equilibrium,

then the system having a tendency to re-establish the equilibrium by undoing the effect we brought.

Consider the following equilibrium.



If O_2 is added and volume of the reaction vessel is reduced, the equilibrium

- (1) Shifts in the product side
 (2) Remains unchanged
 (3) Shifts in the reactant side
 (4) Cannot be predicted
34. If we add CrO_4^{2-} ion to a saturated solution of Ag_2CrO_4 , it will
 (1) Result in an increase in Ag^+ concentration
 (2) Result in a decrease in Ag^+ concentration
 (3) Shift Ag^+ ions from solid Ag_2CrO_4 into solution.
 (4) Result in a decrease the CrO_4^{2-} ion concentration in the solution.
35. Three sparingly soluble salts A_2B , AB , and AB_3 are given. If all the three having the same value of solubility products (K_{sp}), in the saturated solution, the correct order of their solubilities is
 (1) $\text{AB}_3 > \text{AB} > \text{A}_2\text{B}$ (2) $\text{AB}_3 > \text{A}_2\text{B} > \text{AB}$
 (3) $\text{AB} > \text{AB}_3 > \text{A}_2\text{B}$ (4) $\text{AB} > \text{A}_2\text{B} > \text{AB}_3$

Paragraph 12

H_3PO_4 is a tribasic acid with pK_{a_1} , pK_{a_2} and pK_{a_3} 2.12, 7.21, and 12.32, respectively. It is used in fertiliser productions and its various salts are used in food, detergent, toothpaste, and in metal treatment.

Small quantities of H_3PO_4 are used in imparting the sour or tart taste to soft drinks, such as Coca Cola, and beers, in which H_3PO_4 is present 0.05% by weight (density = 1.0 g mL^{-1}).

10^{-3} M H_3PO_4 ($\text{pH} = 7$) is used in fertilisers as an aqueous soil digesting. Plants can absorb zinc in water soluble form only. Zinc phosphate is the source of zinc and PO_4^{3-} ions in the soil. K_{sp} of zinc phosphate = 9.1×10^{-33} .

36. Calculate the pH of a Coca Cola, assuming that the acidity of the cola arises only from H_3PO_4 and K_{a_2} and K_{a_3} are of no importance.
 (1) 1.8 (2) 2.2 (3) 3.3 (4) 4.4
37. $[\text{PO}_4^{3-}]$ ion in the soil with $\text{pH} = 7$, is
 (1) 10^{-3} M (2) $1.2 \times 10^{-4} \text{ M}$
 (3) $2.2 \times 10^{-4} \text{ M}$ (4) $1.1 \times 10^{-10} \text{ M}$
38. $[\text{Zn}^{2+}]$ ion in the soil is
 (1) $2.9 \times 10^{-11} \text{ M}$ (2) $4.0 \times 10^{-10} \text{ M}$
 (3) $3.0 \times 10^{-6} \text{ M}$ (4) $9.1 \times 10^{-5} \text{ M}$

Paragraph 13

Aqueous solutions of $\text{Na}_2\text{C}_2\text{O}_4$ and CaCl_2 are mixed and precipitate of CaC_2O_4 formed is filtered and dried. 250 mL of the saturated

solution of CaC_2O_4 required 6.0 mL of 0.001 M KMnO_4 solution in acidic medium for complete titration.

39. Number of mol of KMnO_4 required is this titration and number of mol of $\text{C}_2\text{O}_4^{2-}$ ion present in the given saturated solution of CaC_2O_4 respectively are

- (1) 6×10^{-6} , 6×10^{-6} (2) 6×10^{-6} , 1.5×10^{-5}
 (3) 1.5×10^{-5} , 6×10^{-6} (4) 6×10^{-6} , 3×10^{-6}

40. Equivalent of KMnO_4 required in the titration and equivalent of $\text{C}_2\text{O}_4^{2-}$ ion present in CaC_2O_4 , respectively, are

- (1) 3×10^{-5} , 3×10^{-5} (2) 1.8×10^{-5} , 3×10^{-6}
 (3) 3×10^{-6} , 6×10^{-6} (4) 6×10^{-6} , 3×10^{-6}

41. K_{sp} of CaC_2O_4 is

- (1) 2.25×10^{-12} (2) 2.25×10^{-10}
 (3) 3.6×10^{-9} (4) 4.0×10^{-9}

42. Which is the indicator in the above titration?

- (1) Phenolphthalein (2) Methyl orange
 (3) KMnO_4 itself (4) None

Paragraph 14

HIn is an acidic indicator ($K_{\text{Ind}} = 10^{-7}$) which dissociates into aqueous acidic solution of 30 mL of 0.05 M H_3PO_4 ($K_1 = 10^{-3}$, $K_2 = 10^{-7}$, $K_3 = 10^{-13}$)

43. Calculate the $\left[\frac{\text{Ind}^\ominus}{\text{HIn}} \right]$

- (1) 1.413×10^{-5} (2) 1.413×10^{-4}
 (3) 3.128×10^{-5} (4) 3.128×10^{-14}

44. If HIn and Ind^\ominus possess colour P and Q, respectively, and colour P predominates over colour Q when the concentration of HIn is 120 times than that of Ind^\ominus . Colour Q predominates over P when concentration of Ind^\ominus is 127 times of HIn.

What is the pH range of the indicator.

- (1) 4.896 to 9.0792 (2) 4.896 to 8.0792
 (3) 4.896 to 7.0792 (4) 4.896 to 6.0792

45. If this solution is treated with 30 mL of NaOH solution, then what molarity of NaOH is needed to reach the equivalence point with indicator?

- (1) 0.1 M (2) 0.2 M (3) 0.3 M (4) 0.4 M

Matrix Match Type

This section contains questions each with two columns—I and II. Match the (salt solution) given in column I with that pH in column II.

1.	Column I (Salt solution)	Column II (pH)
a.	0.1 M KCN	p. 7
b.	$0.1 \text{ M Ph NH}_3^\oplus \text{Cl}^\ominus$	q. $6.5 + \frac{1}{2} \text{p}K_a$
c.	0.1 M KCl	r. $7.5 - \frac{1}{2} \text{p}K_b$
d.	$0.1 \text{ M CH}_3\text{COONH}_4 (K_a = K_b)$	s. $7.5 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$

2.	Column I (Solutions)	Column II (Characteristics)
a.	$0.1 \text{ M CH}_3\text{COOH}$ ($\text{p}K_a = 4.74$) + $0.1 \text{ M CH}_3\text{COONa}$	p. Acidic buffer at its maximum capacity
b.	$0.1 \text{ M CH}_3\text{COOH}$ + 0.1 M HCl	q. Buffer solution
c.	$0.1 \text{ M CH}_3\text{COOH}$ ($\text{p}K_a = 4.74$) + $0.1 \text{ M NH}_4\text{OH}$ ($\text{p}K_b = 4.74$)	r. $\text{pH} < 7$ at 25°C
d.	300 mL of $0.1 \text{ M CH}_3\text{COONa}$ + 100 mL of 0.1 M HCl	s. $\text{pH} = 7$ at 25°C

3.	Column I	Column II
	Sparingly soluble salt	Solubility
a.	Solubility of AgCl in 0.1 M HCl	p. $\frac{K_{sp}}{(0.1)^2}$
b.	Solubility of Ni(OH)_2 in 0.1 M NaOH	q. $\frac{K_{sp}}{0.1}$
c.	Solubility of Ni(OH)_2 in NiCl_2	r. $\frac{K_{sp}}{(0.1)^3}$
d.	Solubility of Al(OH)_3 in 0.1 M NaOH	s. $\left(\frac{K_{sp}}{4 \times 0.1} \right)^{1/2}$
e.	Solubility of AgCN in a buffer solution of $\text{pH} = 3$	t. $\left[K_{sp} \left(1 + \frac{H^\oplus}{K_a} \right) \right]^{1/2}$

4.	Column I	Column II
a.	Acidic salt	p. $\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$
b.	Basic salt	q. $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_b + \log C)$
c.	Acidic buffer	r. $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$
d.	Basic buffer	s. $\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Base}]}$

5.	Column I	Column II
a.	NH_4Cl in water	p. Neutral solution which does not undergo hydrolysis
b.	CH_3COONa in water	q. Cationic hydrolysis
c.	NH_4CN in water	r. Anionic hydrolysis
d.	NaCl in water	s. Both cationic and anionic hydrolysis

6.	Column I	Column II
a.	$10^{-2} \text{ M } (\text{NH}_4)_2 \text{SO}_4$ solution	p. Cationic hydrolysis
b.	10^{-2} M HCl solution	q. Anionic hydrolysis
c.	10^{-2} M NH_3 solution	r. pH changes by one unit when diluted to one-tenth of its concentration
d.	$10^{-2} \text{ M CH}_3\text{COONH}_4$ solution	s. $\text{pH} < 7$ at 25°C

7.	Column I	Column II
	Sparingly soluble salt of weak acid	Ratio of solubilities of salt in buffer and in H_2O
a.	Ratio of solubility of a salt MCN in a buffer of $\text{pH} = 3$, ($K_a = 10^{-3}/3$) and solubility in H_2O is	p. 4
b.	Ratio of solubility of a salt MCN in a buffer of $\text{pH} = 4$, ($K_a = 10^{-4}/7$) and solubility in H_2O is	q. 2
c.	Ratio of solubility of a salt MCN in a buffer of $\text{pH} = 5$ ($K_a = 10^{-5}/8$) and solubility in H_2O is	r. 8
d.	Ratio of solubility of AgCl in 0.1 M HCl and 0.2 M AgNO_3 .	s. 3
e.	Ratio of solubility of $\text{Al}(\text{OH})_3$ in 0.1 M HCl and 0.2 M NaOH .	

8. 50.0 mL of $0.1 \text{ M CH}_3\text{COOH}$ solution is taken to which the following quantities of 0.1 M NaOH have been added. Match the followings.

Column I	Column II
Volume of 0.1 M NaOH added to 50 mL of $0.1 \text{ M CH}_3\text{COOH}$ ($\text{p}K_a \text{ CH}_3\text{COOH} = 4.74$)	pH of solution
a. 25.0 mL	p. 5.34
b. 40.0 mL	q. 11.96
c. 50.0 mL	r. 4.74
d. 60.0 mL	s. 12.22
e. 70.0 mL	t. 8.72

9. 100 mL of $0.01 \text{ M H}_2\text{S}$ solution is taken to which the following quantities of 1.0 M NaOH have been added. $K_1(\text{H}_2\text{S}) = 10^{-7}$, $K_2(\text{HS}^-) = 10^{-14}$. Match the following.

Column I	Column II
Volume of NaOH added	pH
a. 0.0 mL	p. 7.0
b. 0.5 mL	q. 4.5
c. 1.0 mL	r. 9.5
d. 1.5 mL	s. 11.7
	t. 12.0

10. 1.0 L of 0.01 M NH_3 solution is taken to which the following quantities of 1.0 M HCl is added. ($\text{p}K_b(\text{NH}_3) = 4.74$). Match the followings.

Column I	Column II
Volume of HCl added	pOH
a. 2.0 mL	p. 11.0
b. 5.0 mL	q. 4.14
c. 10.0 mL	r. 4.74
d. 11.0 mL	s. 8.37

11.	Column I	Column II
	Species	Characteristic
a.	HSO_4^-	p. Lewis acid
b.	BF_3	q. Lewis base
c.	$\ddot{\text{N}}\text{H}_3$	r. Bronsted acid
d.	OH^-	s. Bronsted base

12.	Column I	Column II
	Type of titration	Indicator
a.	$\text{NaOH} + \text{HCl}$	p. Phenolphthalein
b.	$\text{H}_2\text{SO}_4 + \text{NH}_4\text{OH}$	q. Phenol red
c.	$\text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$	r. Bromocresol green
d.	$\text{KOH} + \text{H}_2\text{SO}_4$	s. Methyl orange

13.	Column I	Column II
	Statements	Characteristics
a.	Hydrolysis of ethyl acetate in basic solution	p. Second-order reaction
b.	Hydrolysis of ethyl acetate in acidic solution	q. First-order reaction.
c.	The limits of pH values of a buffer solution.	r. $\text{p}K_a \neq 1$
d.	The buffer capacity of a solution is maximum when the concentration of salt to the acid is	s. Equal

Column I	Column II
Solubility is x M	K_{sp}
a. $\text{Li}_3\text{Na}_3 (\text{AlF}_6)_2$	p. $108x^5$
b. Zirconium phosphate	q. $2916x^8$
c. Bismuth (III) sulphide	r. $27x^4$
d. Aluminium hydroxide	s. $4x^3$
e. Calcium fluoride	t. $6912x^7$

Numerical Value Type

1. What is the sum of magic numbers of all solutions given below: (Integer value is between 50 and 60)

(Magic number of a solution = pH of solution \times Weight factor)

Solution	Weight factor
I 0.1 M HCN ($K_a = 10^{-10}$)	2
II 0.1M CH_3COOH + 0.1M CH_3COONa ($K_a = 10^{-5}$)	1
III 0.1 M HCl	3
IV 0.1 M NH_4OH ($K_b = 10^{-5}$)	2
V 0.01 M NaOH	0.5
VI 10 mL of 0.1 M CH_3COOH + 10 mL of 0.1 M NH_4OH	1

2. How many of the following cations belong to group IIA, III, IV, and V only in qualitative salt analysis?

Sn^{2+} , Hg_2^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} , Cr^{3+} , As^{3+} , Mg^{2+} , Sb^{3+}

3. How many of the following are strong electrolytes?

a. NH_3 b. NH_4Cl c. CH_3COOH
d. CH_3COONa e. HCl f. NaCl

4. How many of the following 0.1 M solutions are acidic?
a. NH_4Cl b. NaOH c. $\text{HC}_2\text{H}_3\text{O}_2$ d. NaCl
e. $\text{NH}_3 + \text{NH}_4\text{Cl}$ f. NH_3 g. HCl
h. HClO_4 i. $(\text{NH}_4)_2\text{SO}_4$ j. K_2SO_4

5. How many in Q. (4) are basic?

6. How many in Q. (4) are neutral?

7. How many of the following salts:

i. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ii. PhCOONH_4 iii. $\text{NaC}_2\text{H}_3\text{O}_2$
iv. NH_4Cl v. MgS vi. Na_2SO_4
vii. KCl

- a. Hydrolyse more in water at 25°C .

- b. Do not hydrolyse.

- c. Both cation and anion hydrolyse to the same extent.

- d. Both cation and anion hydrolyse to different extent.

8. How many of the following combinations of reactants will react less than 2% of theoretically possible extent?

a. $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$ b. $\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$

c. $\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$ d. $\text{CH}_3\text{COOH} + \text{KOH}$

e. $\text{CH}_3\text{COOK} + \text{HCl(aq)}$ f. $\text{HCl(g)} + \text{H}_2\text{O}$

g. $\text{Cl}^- + \text{H}_3\text{O}^+$

h. $\text{Cl}^- + \text{H}_2\text{O}$

i. $\text{NH}_4^+ + \text{KOH}$

j. $\text{NH}_4^+ + \text{OH}^-$

k. $\text{NH}_3 + \text{H}_2\text{O}$

l. $\text{NH}_3 + \text{H}_3\text{O}^+$

m. $\text{NH}_3 + \text{HCl(aq)}$

n. $\text{K}^+ + \text{OH}^-$

9. How many of the combinations of reactants in Q. (8) above will react until more than 98% of the limiting quantity is used up?

10. Calculate the pH at equilibrium point when a solution of 10^{-6} M CH_3COOH is titrated with a solution of 10^{-6} M NaOH. K_a for acid 2×10^{-5} ($\text{p}K_a = 4.7$) (Answer given in whole number).

Archives

JEE MAIN

Single Correct Answer Type

1. An acid HA ionizes as $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$. The pH of 1.0 M solution is 5. Its dissociation constant would be

(1) 1×10^{-10} (2) 5
(3) 5×10^{-8} (4) 1×10^{-5} (AIEEE 2009)

2. Three reactions involving H_2PO_4^- are given below:

I. $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$

II. $\text{H}_3\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$

III. $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_3\text{PO}_4 + \text{O}^{2-}$

In which of the above does H_2PO_4^- act as an acid?

(1) II only (2) I and II
(3) III only (4) I only (AIEEE 2010)

3. In aqueous solution, the ionization constants for carbonic acid are

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

(1) The concentration of CO_3^{2-} is 0.034 M

(2) The concentration of CO_3^{2-} is greater than that of HCO_3^-

(3) The concentration of H^+ and HCO_3^- are approximately equal

(4) The concentration of H^+ is double that of CO_3^{2-}
(AIEEE 2010)

4. Solubility product of silver bromide is 5.0×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is

(1) $1.2 \times 10^{-10} \text{ g}$ (2) $1.2 \times 10^{-9} \text{ g}$
(3) $6.2 \times 10^{-5} \text{ g}$ (4) $5.0 \times 10^{-8} \text{ g}$ (AIEEE 2011)

5. At 25°C , the solubility product of $\text{Mg}(\text{OH})_2$ is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions?

(1) 9 (2) 10
(3) 11 (4) 8 (AIEEE 2012)

6. Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} \text{ M}$ Na_2CO_3 solution. At what concentrations of Ba^{2+} , will a precipitate begin to form?

(K_{sp} for $\text{BaCO}_3 = 5.1 \times 10^{-9}$)

(1) $4.1 \times 10^{-5} \text{ M}$ (2) $5.1 \times 10^{-5} \text{ M}$
(3) $8.1 \times 10^{-8} \text{ M}$ (4) $8.1 \times 10^{-7} \text{ M}$

(JEE Main 2014)

7. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is:

(1) 7.2 (2) 6.9
(3) 7.0 (4) 1.0 (JEE Main 2017)

8. Which of the following salts is the most basic in aqueous solution?

(1) CH_3COOK (2) FeCl_3
(3) $\text{Pb}(\text{CH}_3\text{COO})_2$ (4) $\text{Al}(\text{CN})_3$

(JEE Main 2018)

9. Which of the following are Lewis acids?

(1) AlCl_3 and SiCl_4 (2) PH_3 and SiCl_4
(3) BCl_3 and AlCl_3 (4) PH_3 and BCl_3

(JEE Main 2018)

10. A aqueous solution contains an unknown concentration of Ba^{2+} . When 50 mL of a 1 M solution of Na_2SO_4 is added, BaSO_4 just begins to precipitate. The final volume is 500 mL. The solubility product of BaSO_4 is 1×10^{-10} . What is the original concentration of Ba^{2+} ?

(1) $2 \times 10^{-9} \text{ M}$ (2) $1.1 \times 10^{-9} \text{ M}$

LIST-I

1. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid diluted to 60 mL)
2. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid diluted to 80 mL)
3. (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL
4. 10 mL saturated solution of $\text{Ni}(\text{OH})_2$ in equilibrium with excess solid $\text{Ni}(\text{OH})_2$ is diluted to 20 mL (solid $\text{Ni}(\text{OH})_2$ is still present after dilution).

LIST-II

1. the value of $[\text{H}^+]$ does not change on dilution
2. the value of $[\text{H}^+]$ changes to half of its initial value on dilution
3. the value of $[\text{H}^+]$ changes to two times of its initial value on dilution
4. the value of $[\text{H}^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
5. the value of $[\text{H}^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

(3) $1.0 \times 10^{-10} \text{ M}$

(4) $5 \times 10^{-9} \text{ M}$

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates.

(1) CuS and HgS (2) MnS and CuS
(3) MnS and NiS (4) NiS and HgS

(IIT-JEE 2011)

2. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

(1) 0.9 L (2) 2.0 L (3) 9.0 L (4) 0.1 L

(JEE Advanced 2013)

3. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is

(1) 1.1×10^{-11} (2) 1.1×10^{-10}
(3) 1.1×10^{-12} (4) 1.1×10^{-9}

(JEE Advanced 2013)

4. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is $1/100^{\text{th}}$ of that of a strong acid (HX, 1M), at 25°C . The K_a of HA is

(1) 1×10^{-4} (2) 1×10^{-5}
(3) 1×10^{-6} (4) 1×10^{-3}

(JEE Advanced 2013)

Multiple Correct Answers Type

1. Aqueous solutions of HNO_3 , KOH, CH_3COOH , and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is/are

(1) HNO_3 and CH_3COOH
(2) KOH and CH_3COONa
(3) HNO_3 and CH_3COONa
(4) CH_3COOH and CH_3COONa

(IIT-JEE 2010)

Matrix Match Type

1. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solutions on $[\text{H}^+]$ are given in LIST-II.

(Note: Degree of dissociation (α) of weak acid and weak base is $\ll 1$; degree of hydrolysis of salt $\ll 1$; $[\text{H}^+]$ represents the concentration of H^+ ions)

Match each process given in LIST-I, with one or more effect(s) in LIST-II. The correct option is

- (1) $P \rightarrow 4; Q \rightarrow 2; R \rightarrow 3; S \rightarrow 1$
 (2) $P \rightarrow 4; Q \rightarrow 3; R \rightarrow 2; S \rightarrow 3$
 (3) $P \rightarrow 1; Q \rightarrow 4; R \rightarrow 5; S \rightarrow 3$
 (4) $P \rightarrow 1; Q \rightarrow 5; R \rightarrow 4; S \rightarrow 1$

(JEE Advanced 2018)

Numerical Value Type

1. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . Find the pH of a 0.01 M solution of its sodium salt. (IIT-JEE 2009)

2. Among the following, find the total number of compounds whose aqueous solution turns red litmus paper blue

KCN, K_2SO_4 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NaCl, $\text{Zn}(\text{NO}_3)_2$, FeCl_2 ,

K_2CO_3 , NH_4NO_2 , LiCN.

(IIT-JEE 2010)

3. Find the total number of diprotic acids among the following:

H_3PO_4 , H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_3BO_3 , H_3PO_2 , H_2CrO_4 , H_2SO_3

(IIT-JEE 2010)

4. In 1 L saturated solution of AgCl (K_{sp} of AgCl = 1.6×10^{-10}), 0.1 mol of CuCl (K_{sp} CuCl = 1.0×10^{-6}) is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . Calculate the value of x . (IIT-JEE 2011)

5. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3} \text{ mol L}^{-1}$. The value of Y is ____.

(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8})

(JEE Advanced 2018)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|----------|----------|----------|----------|----------|
| 1. (1) | 2. (4) | 3. (2) | 4. (3) | 5. (3) |
| 6. (3) | 7. (2) | 8. (2) | 9. (3) | 10. (3) |
| 11. (1) | 12. (3) | 13. (2) | 14. (2) | 15. (3) |
| 16. (4) | 17. (1) | 18. (1) | 19. (2) | 20. (2) |
| 21. (1) | 22. (3) | 23. (1) | 24. (2) | 25. (2) |
| 26. (3) | 27. (2) | 28. (1) | 29. (3) | 30. (1) |
| 31. (1) | 32. (4) | 33. (3) | 34. (3) | 35. (1) |
| 36. (2) | 37. (2) | 38. (3) | 39. (1) | 40. (2) |
| 41. (2) | 42. (3) | 43. (3) | 44. (1) | 45. (1) |
| 46. (4) | 47. (3) | 48. (4) | 49. (1) | 50. (3) |
| 51. (2) | 52. (3) | 53. (3) | 54. (4) | 55. (4) |
| 56. (3) | 57. (4) | 58. (4) | 59. (1) | 60. (4) |
| 61. (2) | 62. (3) | 63. (1) | 64. (3) | 65. (2) |
| 66. (2) | 67. (1) | 68. (1) | 69. (1) | 70. (1) |
| 71. (3) | 72. (2) | 73. (4) | 74. (1) | 75. (3) |
| 76. (4) | 77. (2) | 78. (2) | 79. (2) | 80. (4) |
| 81. (2) | 82. (4) | 83. (1) | 84. (4) | 85. (4) |
| 86. (3) | 87. (1) | 88. (2) | 89. (2) | 90. (1) |
| 91. (4) | 92. (1) | 93. (4) | 94. (2) | 95. (1) |
| 96. (4) | 97. (1) | 98. (4) | 99. (1) | 100. (3) |
| 101. (4) | 102. (2) | 103. (1) | 104. (2) | 105. (1) |
| 106. (3) | 107. (1) | 108. (2) | 109. (1) | 110. (1) |

111. (3) 112. (2) 113. (1) 114. (2) 115. (4)
 116. (3) 117. (4) 118. (2) 119. (3) 120. (3)
 121. (4)

Multiple Correct Answers Type

1. (1, 3) 2. (2, 3, 4) 3. (1, 2) 4. (1, 2)
 5. (1, 2, 4) 6. (1) 7. (4) 8. (2)
 9. (2, 4) 10. (2, 4) 11. (1, 2) 12. (1, 2)
 13. (3) 14. (2, 4) 15. (1, 2, 3) 16. (1, 3)
 17. (1, 2, 3) 18. (1, 3) 19. (1, 2) 20. (1, 3)
 21. (2, 3, 4) 22. (1, 2, 4) 23. (2, 4) 24. (2, 3)
 25. (1, 2, 4) 26. (1, 2, 3, 4) 27. (2, 3) 28. (1, 2, 3)
 29. (1, 2, 3, 4) 30. (1, 2, 3) 31. (2, 3) 32. (2)
 33. (1, 3)

Linked Comprehension Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (2) | 2. (4) | 3. (3) | 4. (2) | 5. (4) |
| 6. (2) | 7. (3) | 8. (4) | 9. (3) | 10. (3) |
| 11. (1) | 12. (1) | 13. (1) | 14. (1) | 15. (1) |
| 16. (3) | 17. (1) | 18. (3) | 19. (1) | 20. (1) |
| 21. (2) | 22. (3) | 23. (2) | 24. (1) | 25. (4) |
| 26. (2) | 27. (1) | 28. (3) | 29. (1) | 30. (4) |
| 31. (3) | 32. (1) | 33. (1) | 34. (2) | 35. (4) |
| 36. (2) | 37. (3) | 38. (1) | 39. (2) | 40. (1) |
| 41. (3) | 42. (3) | 43. (1) | 44. (1) | 45. (1) |

Matrix Match Type

Q.No.	a	b	c	d	e
1.	q	r	p	p, s	—
2.	p	r	s	q	—
3.	q	p	s	r	t
4.	p	q	s	r	—
5.	q	r	s	p	—
6.	p, t	s, t	r	p, q	—
7.	q	p	s	q	r
8.	r	q	t	q	s
9.	q	p	r, t	s	—
10.	q	r	s	p	—
11.	r, s	p	q, s	q, s	—
12.	p, s	r	q	p, s, q	—
13.	p	q	r	s	—
14.	q	t	p	r	s

Numerical Value Type

1. (54) 2. (4) 3. (4) 4. (5) 5. (2)

6. (3) 7. (3, 2, 1, 1)
8. (6) 9. (8) 10. (7)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (1) 2. (1) 3. (3) 4. (2) 5. (2)
6. (2) 7. (2) 8. (1) 9. (3) 10. (2)

JEE Advanced**Single Correct Answer Type**

1. (1) 2. (3) 3. (2) 4. (1)

Multiple Correct Answers Type

1. (3, 4)

Matrix Match Type

1. (4)

Numerical Value Type

1. (8) 2. (3) 3. (6)
4. (7) 5. (4.47)